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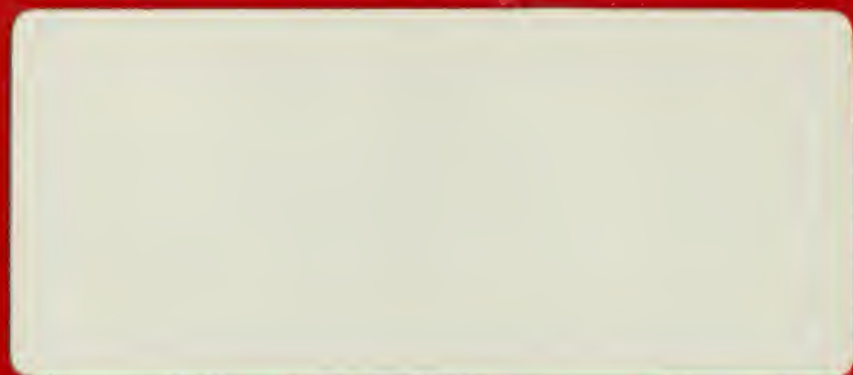


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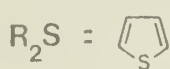
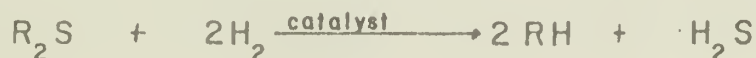


# Synthesis of Molecular Models of Hydrodesulfurization Catalysts

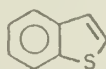
Charles J. Ruffing

August 23, 1984

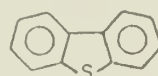
The removal of thiophenes and dibenzothiophenes from petroleum by catalytic hydrodesulfurization (HDS) is becoming increasingly important to fossil fuel processing. The reaction is catalyzed by a cobalt-molybdenum sulfide (eq. 1) and is believed to involve



thiophene



benzothiophene



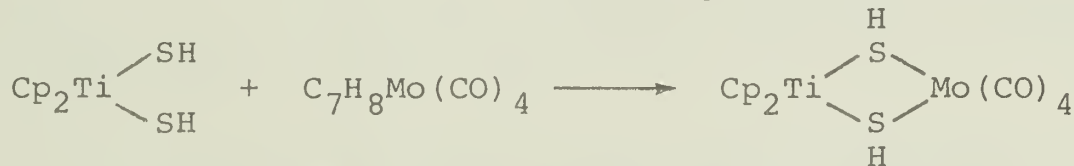
dibenzothiophene

thiophene coordination to the metal surface and subsequent hydrogen transfer from an M-SH (metallothiol) unit to the bound substrate [1]. Transition metal complexes with SH or thiophene ligands may be thought of as molecular analogs of these surface species.

## I. Metallothiols

The reactivity of the metallothiols  $Cp_2M(SH)_2$  ( $M = Ti, W$ ) [2,3] was observed to differ depending on the metal center. While the titanium compound was relatively unreactive, the tungsten compound was readily alkylated by methyl iodide.  $Cp_2W(SH)_2$  also reacted with a methyl isonitrile ligand of  $[Pd(CH_3NC)_2dppe](PF_6)_2$  to afford the dithiocarbamate complex  $[Cp_2WS_2CN(H)CH_3]PF_6$  [4]. This reaction does not occur with uncoordinated methyl isonitrile and illustrates a bimetallic activation of the substrate. The palladium product of this reaction was identified as  $[Pd(CH_3NC)dppe]_2(PF_6)_2$  [5].

The compound  $Cp_2Ti(SH)_2$  functions as a bidentate ligand to form mixed-metal derivatives with bridging SH ligands (eq. 2) [6].



Dynamic NMR spectroscopy established the inversion barrier at sulfur is similar to other ( $\mu$ -SR) derivatives ( $74 \text{ kJ} \cdot \text{mol}^{-1}$ ).

The reactivity of the dimeric Ti-Mo compound increased in relation to the monomeric titanium precursor.  $Cp_2Ti(SH)_2Mo(CO)_4$  was readily alkylated to afford  $Cp_2Ti(SR)_2Mo(CO)_4$ , and reacted with activated olefins to afford the conjugate addition products. The increased reactivity of the thiol groups of the bimetallic compound may be related to the observed bimetallic effect of the HDS catalyst.





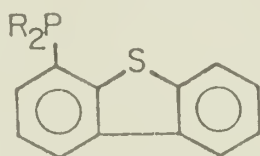
## II. Metal-Thiophene Complexes

In order to induce thiophene coordination to a metal center, several transition metal complexes of the substituted cyclopentadiene ThCpH were prepared and studied spectroscopically. Although



no interaction of thiophene was seen in several complexes of titanium and molybdenum, the compound (ThCp)Ru(PPh<sub>3</sub>)<sub>2</sub>Cl reacts with silver (I) salts to afford a cationic complex whose spectroscopic characteristics are consistent with an S-bound thiophene unit.

The chelating phosphine ligand tol<sub>2</sub>PDBT reacted with Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>



R = 4-MePh; tol<sub>2</sub>PDBT

to afford the transition metal derivative RuCl<sub>2</sub>(tol<sub>2</sub>PDBT)<sub>2</sub>, which was characterized by single crystal x-ray diffraction [7]. This is the first unambiguous example of a metal complex with an S-bound thiophene.

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The Mechanism of Olefin Oxidations  
by an Oxygen-binding Cobalt Complex

Dorothy Hamilton

Final Seminar

September 6, 1984

Oxidations are key steps in the industrial synthesis of most compounds made. Therefore understanding the mechanisms by which these types of reactions occur is important not only synthetically but also commercially. In many cases oxidations are catalyzed by transition metal complexes to overcome kinetic sluggishness as well as to control the number of products formed. Previous work in this group has centered on the activation of dioxygen toward oxidation of substituted phenols by binding to a cobalt Schiff-base complex.[1] In the course of this work it was found that this complex, cobalt bis(salicylidene- $\gamma$ -iminopropyl)methylamine, abbreviated CoSMDPT, was also able to oxidize terminal olefins to form methyl ketones and the corresponding secondary alcohols catalytically.[2] The mechanism of this reaction was investigated.

Many homogeneous oxidations catalyzed by transition metal complexes, especially involving first row metals, proceed by autoxidation, or free radical chain pathways. When olefins are the substrates a variety of products are formed including allylic ketones, alcohols, and hydroperoxides, rather than the methyl ketones and carbinols observed for the CoSMDPT-catalyzed reaction. Experiments were conducted to rule out this most common mechanism, as well as a Wacker-type pathway [3] and the involvement of peracids in the oxidation.

Neither peracids nor superoxide ion could replace dioxygen as the oxidant in the system. However, it was found that catalytic oxidation of olefins did take place when hydrogen peroxide was used and the reaction was carried out under argon (or nitrogen), as long as CoSMDPT was also present.

The mechanism proposed for this oxidation involves formation of a cobalt hydroperoxide as the active catalyst in the system, formed either by addition of hydrogen peroxide produced in situ to the five-coordinate cobalt complex or by abstraction of a hydrogen atom from the solvent by the cobalt-dioxygen species. The Co-OOH is then added across the double bond of the alkene in a Markovnikoff fashion and leads to an alkyl hydroperoxide. Subsequent decomposition of the alkyl hydroperoxide by the Haber-Weiss mechanism,[4] involving both Co(II) and Co(III), yields the observed ketone and alcohol products. Deactivation of the catalyst is caused by oxidation of the bis(salicylidene- $\gamma$ -iminopropyl)methylamine ligand as well as formation of a  $\mu$ -peroxocobalt dimer.

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# Characterization of Alumina-Supported Molybdenum-Iridium Clusters

Winston S. Uchiyama

Final Seminar

September 13, 1984

There has been much interest in bimetallic heterogeneous catalysts since the 1940's [1]. The addition of a second less or non-active metal to a monometallic catalyst has often been found to increase activity, promote favorable selectivity and/or enhance durability. A conventional industrial preparation of these catalysts was by bulk mixing of the metal salts or oxides with the supported material, leading to ill-defined surface species. In addition, the metal salts often contained counterions or ligands with elements known to inhibit specific catalytic reactions [2].

Organometallic compounds, commonly metal carbonyls, have recently gained attention as precursors in heterogeneous catalysis [3,4]. They provide better control over the purity and dispersion of supported metal particles by comparison with conventional methods. The use of heteronuclear clusters has added an additional aspect to this expanding field. With these discrete clusters, one has for the first time the potential of controlling surface metal particle stoichiometry. This may allow one to discern the role of components in a bimetallic catalyst, and perhaps effectively create catalysts with the optimal mixed-metal composition and/or structure. Applications have been limited due, in part, to a lack of suitable compounds [5].

The compounds  $(\eta^5\text{-C}_5\text{H}_5)_x\text{M}_x\text{Ir}_{4-x}(\text{CO})_{12-x}$  ( $\text{M} = \text{Mo}, \text{W}; x = 1, 2$ ) have previously been prepared by Foote [3]. The crystal structures of the tungsten-containing clusters show a tetrahedral core of metal atoms. The molybdenum-containing clusters are assumed to be isostructural [6]. These compounds have been supported on alumina ( $\text{Al}_2\text{O}_3$ ), with studies of  $\text{W-Ir}/\text{Al}_2\text{O}_3$  initially being carried out by Hardwick [3,7]. The properties of the mixed-metal cluster derived catalysts were compared with those derived from stoichiometric mixtures of  $\text{Ir}_4(\text{CO})_{12}$  and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6$ .

The samples were slowly heated to  $500^\circ\text{C}$  in flowing hydrogen. This activation procedure removed surface carbon in the form of methane. The methane evolution profiles for the mixed-metal samples were different from those of the stoichiometric mixtures. The stoichiometric mixtures appeared to be reacting as separate components on the surface, by comparison with the profiles of  $\text{Mo}_2/\text{Al}_2\text{O}_3$  and  $\text{Ir}_4/\text{Al}_2\text{O}_3$ .

Further characterization of the activated samples included selective chemisorption measurements, reactive thermal desorption of adsorbed carbon monoxide and iridium-based n-butane hydrogenolysis. Both mixed-metal cluster-derived samples exhibited unique properties, not obtainable with the stoichiometric mixtures ( $[\text{Ir}_4 + \text{Mo}_2]/\text{Al}_2\text{O}_3$ ). These properties can be attributed to various mixed-metal interactions.

Direct observation of proposed mixed-metal interactions was carried out by x-ray absorption spectroscopy of the molybdenum K-edge [8]. The x-ray absorption near edge structure (XANES) provided information related to the chemical nature (oxidation state and coordination





sphere) of the absorbing atom. The extended x-ray absorption fine structure (EXAFS) was used to determine the identity, radial distances and coordination number of atoms surrounding the absorbing atom. Results indicate that the mixed-metal cluster precursors did provide molybdenum-metal interactions not obtainable through stoichiometric mixtures. The initial tetrahedral metal core apparently did not remain intact on the alumina surface.

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## Phosphinidene- and Arsinidene-Bridged Transition Metal Clusters

Kevin E. Howard

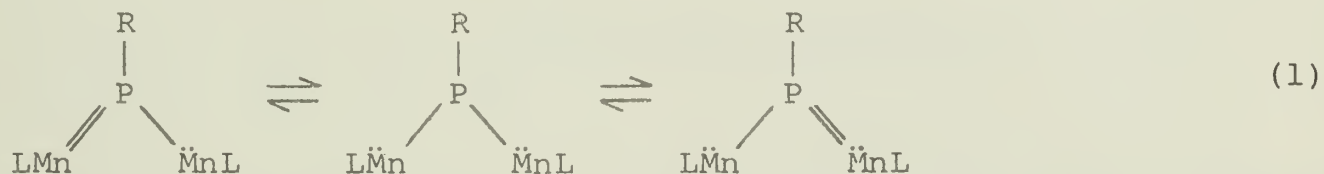
Literature Seminar

October 16, 1984

Phosphinidenes [RP:] were first postulated to occur as reactive intermediates in the reactions of aryl- and alkyl-dichlorophosphines with magnesium or lithium in tetrahydrofuran, yielding cyclic or linear oligomers [1]. Schmidt and Osterroht in 1965 successfully trapped phenylphosphinidene, generated by heating tetraphenylcyclo-tetraphosphine above 160°C or reacting phenyldichlorophosphine with zinc dust at 25°C or oxidizing phenylphosphine with iodine, by insertion into the double bond of diethyldisulfide [2]. Similarly, arsinidenes [RAS:] were postulated by Nefedow and Manakow [3] to act as intermediates during cyclooligoarsane (RAS)<sub>n</sub> formation.

Huttner et. al [4] first reported the stabilization of an arsinidene, phenylarsinidene, in a metal complex in 1975. Soon thereafter, Huttner and coworkers reported similar phenylphosphinidene [5] and phenylstibinidene [6] complexes.

The unusual stability of these complexes arises from the nature of the arsinidene (or phosphinidene or stibinidene) ligand as a four-electron donor, as first described by Huttner [4]. The group VA atom completes its octet of electrons by metal d $\pi$ -pnicogen p $\pi$  back-bonding, while the ligand donates two electron pairs to the metal. The metal-group VA-metal bonding mode is most easily viewed as a 4 $\pi$  electron-3 atom system.



These complexes were the first examples of trigonal planar As(I) and P(I) coordination geometries. The "allylic" nature of these complexes is reflected in unusually short P-metal and As-metal bond distances, as determined by x-ray crystallography [5,7]. Fenske and Kostić recently reported [8] molecular orbital studies on [C<sub>5</sub>H<sub>5</sub>Mn(CO)<sub>2</sub>]<sub>2</sub>PC<sub>6</sub>H<sub>5</sub> which supported the three-center four electron bonding scheme in these complexes.

Inevitably, higher nuclearity phosphinidene, and to a lesser extent arsinidene, clusters have been prepared. Huttner and coworkers have prepared homometallic phosphinidene clusters from M<sub>3</sub>(CO)<sub>12</sub> where M = Fe [9], Ru [10], Os [11]. Geoffroy et. al [12] recently reported the preparation of a  $\mu_4$ -phosphinidene complex which is chemically "attractive" as it contains a catalytically active metal-Rh, labile 1,5-cyclooctadiene ligands, and is coordinately unsaturated. Other researchers have begun investigating mixed-metal phosphinidene clusters containing catalytically active metals such as Ru/Rh [13] and Ru/Au [13].





Investigations into the catalytic behavior of phosphinidene-bridged transition metal clusters have been scarce. Pittman et. al [14] has studied the hydroformylation of pentenes by  $\text{Co}_4(\text{CO})_8-(\mu_4\text{-PC}_6\text{H}_5)_2$  and Cook and Evans [15] have examined the tethering of  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_4\{\mu_3\text{-PCH}_2\text{CH}_2\text{Si}(\text{OEt})_3\}$  on oxide supports. The catalytic potential of phosphinidene-bridged transition metal clusters is an area still open to extensive research.

Most recently, Huttner and coworkers have reported the preparation of new stibinidene complexes of manganese and chromium [16] as well as a phosphinidene chromium complex,  $(\text{Cr}(\text{CO})_5)_2\text{P}(\text{t-butyl})$ , with a  $^{31}\text{P}$ -nmr chemical shift of 1362 ppm (rel. to  $\text{H}_3\text{PO}_4$ ), reported by the authors as the largest  $^{31}\text{P}$ -nmr chemical shift documented to date [17]. Marks et. al [18] have recently prepared and characterized the phosphinidene-bridged actinide methoxy complexes  $[\text{Cp}'_2\text{M}(\text{OCH}_3)]_2\text{PH}$ , where  $\text{Cp}' = \eta^5\text{-(CH}_3)_5\text{C}_5$  and  $\text{M} = \text{Th, U}$ . Jones and Whittlesey [19] reported, this year, the formation of a chromium arsinidene complex which reacts further to form the heterometallacycle  $\text{CrAs}_4$ . Finally Mathey and Marinetti [20] examined the cycloaddition of alkenes to a phosphinidene complex.

Phosphinidene- and arsinidene-bridged transition metal clusters containing a variety of metals have been prepared and structurally characterized. However, the reactivity, both stoichiometric and catalytic, of these complexes has only begun to be investigated and may exhibit a rich and varied chemistry.

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# Bonding and Reactivity of Transition Metal Complexes of Carbon Disulfide

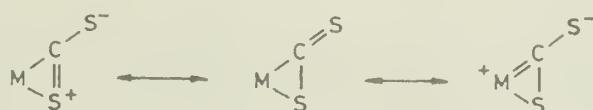
Timothy J. Henly

Literature Seminar

October 23, 1984

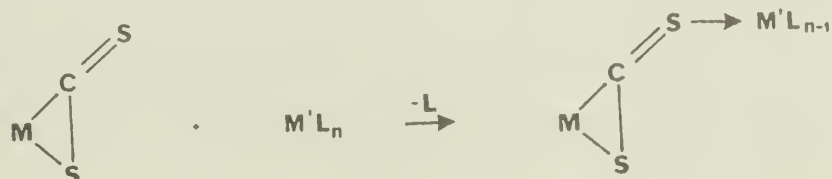
The activation of carbon dioxide by transition metal centers had long been a subject of great interest: if such activation were realized, CO<sub>2</sub> could become an abundant source of reduced C<sub>1</sub> compounds. In spite of intense efforts to induce reactivity, however, CO<sub>2</sub> remains largely inert to transition metals; only a few examples of metal-coordinated CO<sub>2</sub> are known [1]. For this reason, many investigators are now studying the reactions of the more reactive heteroallene carbon disulfide, in the hope that the resulting chemistry might provide some insight into the feasibility of CO<sub>2</sub> activation [2].

The first transition metal-CS<sub>2</sub> complex was prepared by Wilkinson and Baird in 1966 [3]. An X-ray structural determination [4] showed that the CS<sub>2</sub> fragment was  $\pi$ -bonded in a side-on fashion to the metal as shown below:



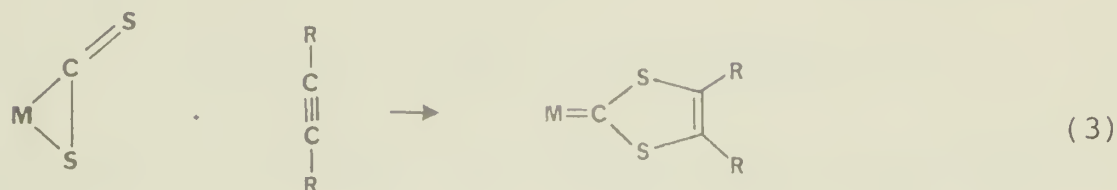
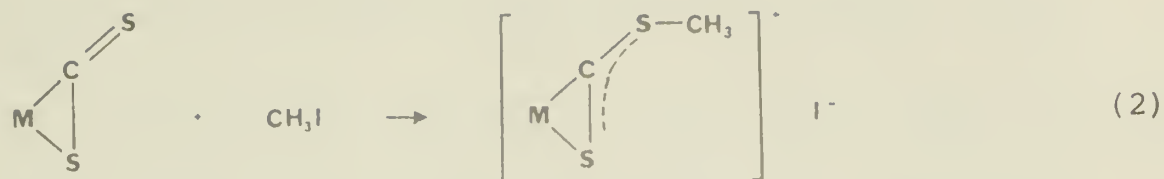
This bonding mode is by far the most common in mononuclear metal-CS<sub>2</sub> compounds; analogous complexes of almost every transition metal have been identified [2]. Several of these complexes have been structurally characterized [5], and the structural data indicate substantial electron delocalization over the MCS<sub>2</sub> system as shown above.

This valence-bond description (and a recent molecular orbital study [6]) indicate that when CS<sub>2</sub> is coordinated to a metal center in this manner, a shift in electron density toward the uncoordinated sulfur atom occurs. The observed reactivity of metal-CS<sub>2</sub> compounds agrees with this description. For example, the exocyclic sulfur can react with another metal center (reaction 1) or with an alkyl halide (reaction 2) to give a heterobinuclear complex or a coordinated dithioester, respectively. The 1,3-dipolar character of the CS<sub>2</sub> moiety is also thought to facilitate cycloadditions with electrophilic alkynes (reaction 3) [7,8,9].



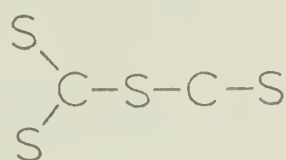
(1)



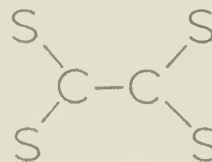


The product of reaction 1 is an example of a CS<sub>2</sub>-bridged binuclear compound. In other structurally characterized binuclear complexes, different bridging modes are seen: the  $\mu$ -CS<sub>2</sub> moiety can donate a total of 2, 4, or 6 electrons to the two metal centers [10,11,7b].

One of the more intriguing aspects of metal-CS<sub>2</sub> chemistry is the recently demonstrated ability of some systems to induce CS<sub>2</sub> coupling. Several examples of head-to-tail coupling (A) [12] and head-to-head coupling (B) [13] have been synthesized and characterized by X-ray crystallography.



(A)



(B)

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# Synthesis of Transition Metal $\pi$ -arene Compounds via Metal Vapors

G. R. Fraunhoffer

Literature Seminar

November 20, 1984

Metal vapor syntheses (MVS) have greatly expanded the number of  $\pi$ -arene compounds of the transition metals and allowed for a systematic study of their chemistry [1]. Fischer's traditional route to  $\pi$ -arenes was both laborious and restricted to a very few arenes [2]. The MVS method, by contrast, is applicable to virtually all metals, even the most refractory (e.g. W), and is suitable for a wide variety of arenes [3].

The MVS technique involves production of metal atoms, usually from either a resistance heated furnace or an electron-gun furnace, and their cocondensation with an arene at low temperature followed by warming and product extraction [1].

Recent studies of  $\pi$ -arene compounds prepared by the MVS method are many and varied. A series of derivatives of  $[\text{Cr}(\text{PhX})(\text{PhCOOH})] - [\text{PF}_6]$  ( $\text{X} = \text{H}, \text{CH}_3, \text{Cl}, \text{CF}_3$ , etc.) have been prepared and transannular effects on, for instance, the  $\text{pK}_a$  of the carboxylic acid group investigated [4]. Until recently, MVS has been the only synthetic route to divalent group VIII arenes. Studies of  $\text{Ni}(\eta^6\text{-toluene}) - (\text{C}_6\text{F}_5)_2$  show it to contain an unusually labile  $\pi$ -arene [5]. The isoelectronic  $\text{Fe}(\eta^6\text{-toluene})(\text{bpy})$  is, however, essentially inert to arene exchange [6].  $\pi$ -arenes of Re dimers have been prepared and some show C-H activation [7].

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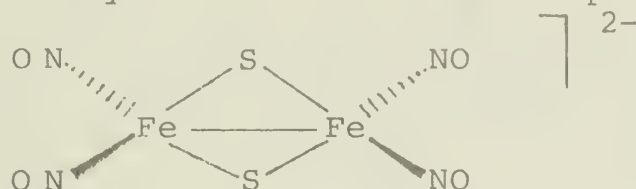
"Roussin's Red Salt Revisited:  
Metal Nitrosyl Dimers and Clusters"

Timothy D. Weatherill

Final Seminar

November 30, 1984

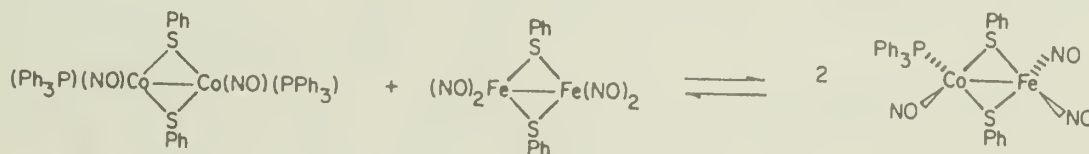
Since its preparation in 1858, "Roussin's Red Salt,"  $M_2Fe_2(\mu-S)_2(NO)_4$  ( $M = Na^+, K^+$ ) [1], has elicited little interest from the inorganic community despite the intense activity in the areas of metal nitrosyls and iron-sulfur compounds.



While our initial investigations into the chemistry of Roussin's Red Salt began as a simple query of the reactivity of this compound towards electrophiles [2], our findings prompted us to investigate the synthesis of metal nitrosyl dimers in general, later evolving into a study of metal nitrosyl clusters.

Metathetical replacement of the bridging iodo ligands in  $Fe_2(\mu-I)_2(NO)_4$  [3] with  $Na_2E$  ( $E = S, Se, Te$ ) was found to be an efficient route to the corresponding Red Salts. Anhydrous solutions of  $Fe_2(\mu-E)_2(NO)_4^{2-}$  could be generated and derivatized with a variety of alkylating or metalating agents. Similarly, the compound  $[Co(NO)_2I]_x$  [3] was found to be a versatile starting material for the esters  $Co_2(\mu-ER)_2(NO)_4$ .

The  $Co_2(\mu-ER)_2(NO)_4$  dimers possess two additional electrons compared to the 34 electron  $Fe_2(\mu-ER)_2(NO)_4$  species; these electrons are assumed to occupy an orbital which is mainly metal-metal anti-bonding. [4] Relative kinetic stabilities of these dimers were studied from the perspective of reactivity. "Mixed esters" of the type  $M_2(\mu-SR)(\mu-SR')(NO)_4$  could be isolated for the formally M-M bonded 34e dimers whereas the 36e mixed esters prove to be too labile to isolate. Extension of the mixed ester synthesis led to the preparation of a mixed-metal dimer:



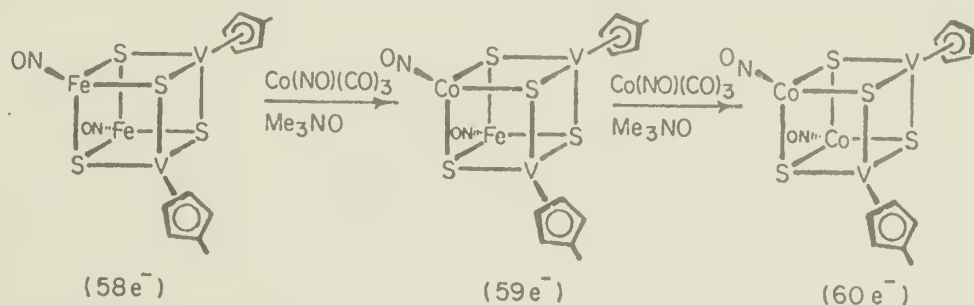
A study of the temperature dependence of the  $K_{eq}$  for this process indicated that the reaction is mildly endothermic, the driving force being a favorable entropy term.

Our studies on metal nitrosyl sulfides were extended to the synthesis of mixed-metal sulfide clusters. The compound  $(MeCp)_2V_2S_4$  exhibits rich and varied coordination chemistry and has been used



to prepare a number of clusters containing both early and late transition metals [5]. In this way complexes of the type  $(\text{MeCp})_2\text{V}_2\text{S}_4 \cdot \text{ML}_n$  were prepared for  $\text{ML}_n = \text{Fe}(\text{NO})_2$ ,  $\text{CoCp}$ ,  $\text{Ir}(\text{PPh}_3)\text{Cl}$ , and  $[\text{Ni}(\text{MeCp})_2\text{V}_2\text{S}_4]$ .

A series of novel, electron deficient cubanes  $(\text{MeCp})_2\text{M}_2\text{S}_4\text{M}'_2 - (\text{NO})_2$  ( $\text{M} = \text{V}, \text{Mo}$ ;  $\text{M}' = \text{Fe}, \text{Co}, \text{Ni}$ ) have been prepared [6]. The  $\text{V}_2\text{S}_4\text{Fe}_2$  cubane undergoes transmetalation with  $\text{Co}(\text{CO})_3\text{NO}$  to produce the hybrid species  $(\text{MeCp})_2\text{V}_2\text{S}_4\text{CoFe}(\text{NO})_2$ :



Other probable cubanes obtained from  $(\text{MeCp})_2\text{V}_2\text{S}_4$  include  $(\text{MeCp})_2 - \text{V}_2\text{S}_4\text{Cr}_2\text{Cp}_2$  and  $(\text{MeCp})_2\text{V}_2\text{S}_4\text{Cu}_2(\text{PPh}_3)_2$ . The structural data for  $\text{V}_2\text{S}_4\text{Fe}_2$ ,  $\text{V}_2\text{S}_4\text{Co}_2$ , and  $\text{V}_2\text{S}_4\text{Ni}_2$  cubanes together with the results of electrochemical and magnetic studies will be discussed.

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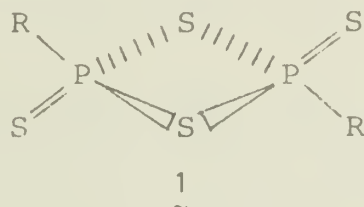
## Sulfur Rich Transition Metal-Main Group Heterocycles and Cages

Gregg A. Zank

Final Seminar

January 17, 1985

The reactivity of elemental sulfur homocycles has long been postulated to occur via highly reactive thiopolysulfide (S=S) ring intermediates [1,2]. The existence of these S=S linkages has been supported by matrix infrared studies [3]. Consistent with the reactivity associated with these postulated S=S intermediates is that observed for the organoperthiophosphinic acid anhydrides, 1.



These anhydrides are one of the most efficient reagents known for the thiation of organic carbonyl compounds (eq. 1) [4,5].



(1)

In an effort to enhance the reactivity of the well studied  $\text{Cp}_2\text{TiS}_5$  system we sought to incorporate  $\text{RP}(\text{S})$  fragments into the pentasulfide ring. As a result of this study a new class of phosphorus sulfide chelates has been prepared, which show a lability analogous to many heterocumulene systems [6]. The transition metal complexes of these phosphorus sulfide chelates were found to have a similar reactivity toward organic substrates as 1, but unlike 1 reacted readily with dioxygen. It is not unusual for titanium complexes to be oxophilic [7], but this reactivity was traced to the lability associated with the particular phosphorus sulfide chelate. The investigation into the reactivity of these transition metal complexes has lead to a better understanding of the reactivity of the parent anhydrides themselves. A kinetics study of the sulfur transfer reactivity of 1 indicated  $\text{RPS}_2$  fragments as the reactive species.

Replacement of the organic group of these organothiophosphoryl ( $\text{RPS}_2$ ) ligands with sulfide affords, formally, condensed anions of trithiophosphite ( $\text{PS}_3^{2-}$ ). Divalent metal salts of these dianions ( $\text{MES}_3$ ,  $\text{E}=\text{P}, \text{As}$ ) have been employed as intercalation hosts [8,9], while mono- and divalent metal salts of the  $\text{ES}_3^{3-}$  trianion form a large class of minerals termed Sulfosalts [10]. In an effort to produce molecular transition metal complexes of these  $\text{ES}_3$  anions, the reactions of two binary arsenic sulfide minerals, Orpiment ( $\text{As}_2\text{S}_3$ ) and Realgar ( $\text{As}_4\text{S}_4$ ), with nucleophiles were investigated. These minerals were found to dissolve in the presence of sulfide which followed by metathesis with organotransition metal halides or through the use of nucleophilic transition metal sulfides has lead to the isolation of molecular compounds. These transition metal compounds can be viewed as molecular Sulfosalts in that they contain  $\text{AsS}_3^{3-}$  or catenates of these trigonal pyramids as ligands.





One of these molecular Sulfosalts ( $\text{Cp}_3\text{Ti}_2\text{OAsS}_3$ ) structurally resembles the  $\text{E}_4\text{S}_3$  ( $\text{E}=\text{P}, \text{As}$ ) cages wherein a  $\text{Cp}_2\text{Ti}$  fragment occupies a divalent site (S) and a  $\text{CpTi}$  moiety a trivalent one (E). This observation suggested the possibility of preparing  $(\text{CpTi})_4\text{S}_x$  cages from mono(cyclopentadienyl)titanium trichloride and lithium sulfides. The two isolated complexes from this reaction were  $\text{Cp}_4\text{Ti}_4\text{S}_8\text{O}_x$  ( $x=1,2$ ) which like the  $\text{E}_4\text{S}_3$  cages are comprised of a tetrahedral array of trivalent atoms. Unlike the main group cages these  $\text{Ti}_4$  compounds contained  $\mu_4$ -oxides and bridging disulfides.

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# Synthesis and Reactivity of Metallacyclobutanes

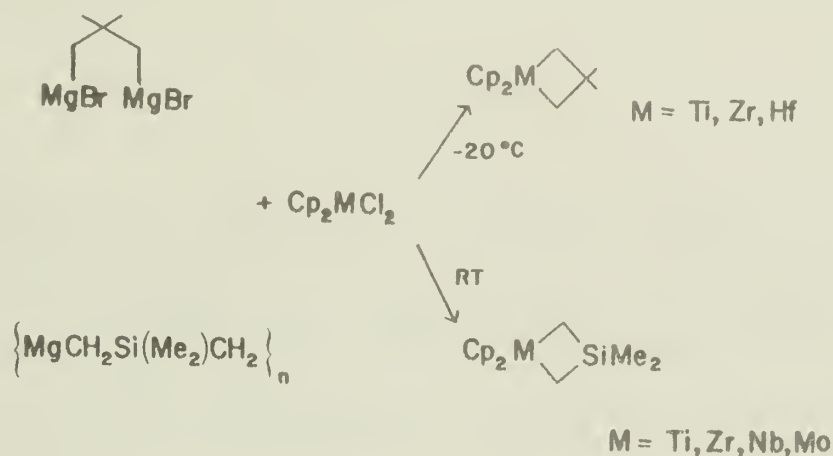
Ann Hermes

Literature Seminar

February 7, 1985

Metallacyclobutanes have been proposed as intermediates in a number of catalytic processes, including olefin metathesis [1], olefin polymerization [2], and alkane isomerization [3]. Due to the intimate involvement of metallacyclobutanes in carbon-carbon bond formation and cleavage reactions, several synthetic routes to isolable metallacyclobutanes have been developed and the reactivity of these compounds has been studied.

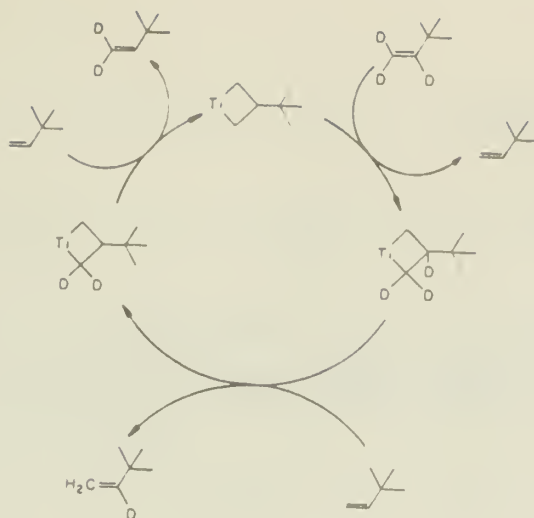
Many metal-specific routes to metallacyclobutanes are available, including oxidative addition of cyclopropane [4], reduction of  $\pi$ -allyl complexes [5],  $\gamma$ -H elimination in bis(neopentyl) complexes [6], and olefin reaction with the Tebbe reagent [7]. Recently Bergman and Periana reported the synthesis of a rhodacyclobutane via the rearrangement of a hydridocyclopropylrhodium complex [8]. Recent synthetic developments in the isolation of digrignard and magnesa-cycle reagents potentially offer a more general route to metallacyclobutanes [9].



With metallacyclobutane complexes in hand, decomposition, isomerization, and reactivity studies have been carried out to gather evidence for the mode of carbon-carbon bond cleavage. Green and coworkers reported that photolytic decomposition of  $\text{Cp}_2\text{WCH}_2\text{CH}_2\text{CH}_2$  produced ethylene [10]. Their proposed mechanism involved a  $\eta^5$  to  $\eta^3$  shift of one cyclopentadienyl ring, followed by cleavage of the metallacycle ring into alkylidene and ethylene fragments, in the manner of the Chauvin mechanism for olefin metathesis [11]. Grubbs and coworkers have studied the isomerization of  $\text{Cp}_2\text{TiCH}_2\text{CHPhCH}_2$  and their results indicate similar metallacycle fragmentation but without the need for the  $\eta^5$  to  $\eta^3$  shift [11]. Puddephatt and Casey have separately studied the isomerization of  $\text{Cl}_2\text{L}_2\text{PtCH}_2\text{CH}_2\text{CHPh}$ . Their results are consistent with a concerted mechanism [12].

Titanacyclobutanes do indeed exchange with olefins and catalyze degenerate metathesis [13].





It has also been shown that titanacyclobutanes react with ketones to produce olefins [14]. Analogous reactions with zircona- and hafnacyclobutanes result in carbonyl insertion into a metal-carbon bond rather than cleavage of a metallacycle carbon-carbon bond [9b].

The new synthetic routes may lead to more, diverse metalla-cyclobutanes and studies of this interesting class of molecules should continue.

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## Electron Transfer in Mixed-Valence Binuclear Ferrocenes

Michael F. Moore

Final Seminar

February 12, 1985

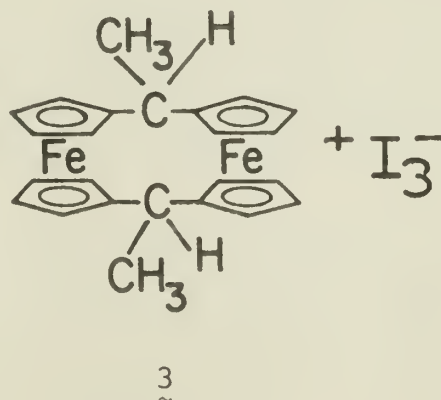
The study of mixed-valence ferrocene complexes could lead to a better understanding of the factors which control the rate of thermal electron transfer in oxidation-reduction, electrochemical, and biological reactions [1].

The mixed-valence monocation of bis(fulvalene)diiron (1) has been fully characterized by a variety of physical techniques [2-4].



The rate of intramolecular thermal electron transfer in this monocation is faster than the  $^{57}\text{Fe}$  Mössbauer and EPR time scales. Hence there is no barrier to electron transfer in this complex. A study was undertaken to determine directly if there is any change in the electron transfer rate resultant upon substitution of a single acetyl group in the 3-position of 1. The acetyl substituent acts as an electron withdrawing group, increasing the oxidation potential of the ferrocenyl unit to which it is attached. This could serve to localize the odd electron of the mixed-valence cation on the unsubstituted half of the molecule.  $^{57}\text{Fe}$  Mössbauer data, EPR data, and IR data collected on the triiodide salt of 2 indicate that this mixed-valence cation has a delocalized ground state.

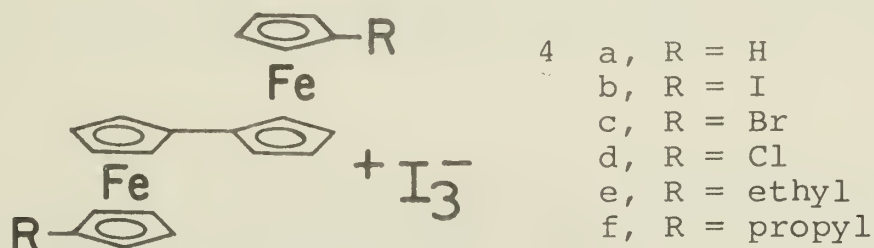
The preparation and characterization of the mixed-valence triiodide salt of 1,12-dimethyl[1.1]-ferrocenophane (3) has been reported [3,5].





$^{57}\text{Fe}$  Mössbauer spectra collected on **3** exhibit both Fe(II) and Fe(III) absorptions. The appearance of an additional quadrupole-split doublet ( $\Delta E_Q = 1.85 \text{ mm/sec}$ ) in the  $^{57}\text{Fe}$  Mössbauer spectra of **3** led to speculation that a separate conformer within the crystal lattice had a delocalized ground state. The single-crystal X-ray structure of **3** was obtained. Only one unique cation is observed for this molecule within the unit cell. Distinguishable Fe(II) and Fe(III) sites in the crystal structure of **3** are consistent with a trapped valence description for this mixed-valence salt. The dioxidized  $(\text{I}_3^-)_2 \cdot \text{I}_2$  salt of **3** was prepared and characterized. A small exchange interaction is seen to develop between the two  $S = \frac{1}{2}$  ions in this dication.

The mixed-valence biferrocenium cation (**4a**) has been shown to be localized on both the  $^{57}\text{Fe}$  Mössbauer and EPR time scales [3,6,7].

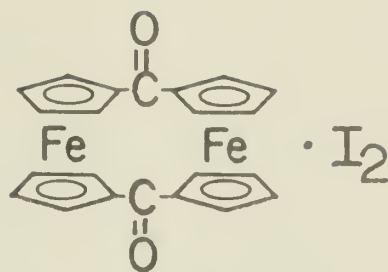


The triiodide salts of 1,6-diiodobiferrocenium (**4b**) and 1,6-dibromobiferrocenium (**4c**) have delocalized ground states as gauged by  $^{57}\text{Fe}$  Mössbauer spectroscopy [3,8]. The triiodide salt of the chlorosubstituted cation (**4d**) is valence localized [8]. Substitution of alkyl groups onto the biferrocenium framework yields mixed-valence compounds which exhibit a temperature dependence of the rate of thermal electron transfer [9]. Compounds **4e** and **4f** are both localized on the  $^{57}\text{Fe}$  Mössbauer time scale below 100 K. At room temperature both of these compounds appear to be delocalized with one average valence quadrupole-split doublet observed in their Mössbauer spectra. An interesting feature of the Mössbauer spectra collected on **4e** and **4f** is the complete absence of line broadening of the Mössbauer signals in going from low temperatures to high temperatures. Variable-temperature EPR and IR spectra were collected for **4e** in an effort to understand the anomalous Mössbauer behavior. A model is proposed which accounts for the lack of line broadening observed in these systems.

Considerable interest has been generated recently in understanding the unusual electronic and magnetic properties associated with quasi-one-dimensional charge-transfer salts [10]. Slow crystallization of 1,12-dione[1.1]ferrocenophane from hot  $\text{CHCl}_3$  solutions in the presence of a twentyfold excess of iodine leads to the formation of lustrous golden crystals of empirical formula  $[(\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}(\text{CO})_2\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2] \cdot \text{I}_2$  (**5**).







5  
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Iodine containing materials are particularly amenable to characterization by Raman spectroscopy [11,12]. A resonance Raman spectrum collected for a solid sample of 5 indicates the iodine present in this salt to be of the form  $(\text{I}_3^-) \cdot \text{I}_2$ . This result suggests that 5 is best formulated as  $[(\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}(\text{CO})_2\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2]_5^{2+} (\text{I}_3^-)_2 \cdot (\text{I}_2)_2$ . Magnetic susceptibility measurements and  $^{57}\text{Fe}$  Mössbauer spectra collected on 5 are consistent with the proposed partial oxidation of this complex. The rate of thermal electron transfer in 5 is less than the  $^{57}\text{Fe}$  Mössbauer and EPR time scales.

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# Selective Oxidations via Metal Oxides: The Relevance of Organometallic Oxo Complexes

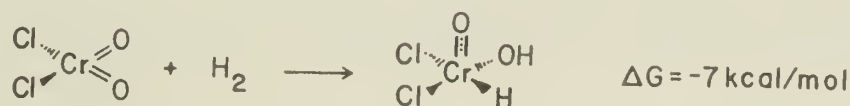
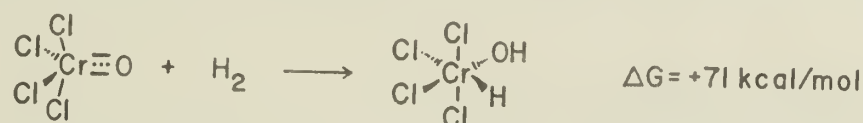
James A. Jensen

Literature Seminar

February 14, 1985

Metal oxides are known for all of the transition metals and such species are known to play a vital role in many important industrial processes, such as olefin metathesis [1], and hydrocarbon oxidations [2,3]. In most of these processes, organometallic oxo derivatives are key intermediates, however, relatively few isolated examples of complexes containing metal-oxo and metal-carbon bonds are known [4-10].

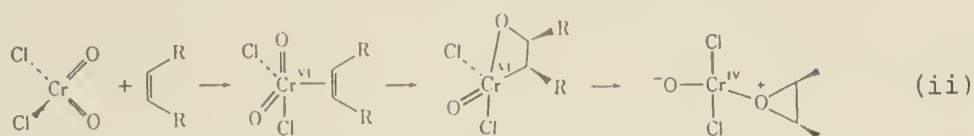
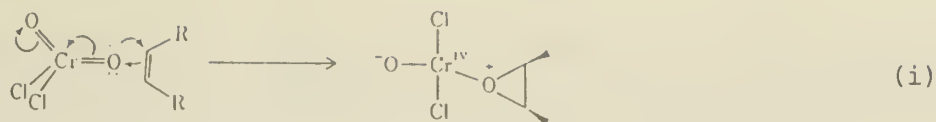
Terminal oxide ligands are strong electron donors to transition metals both in a  $\sigma$  and a  $\pi$  sense. The metal-oxygen linkages are generally considered to be double bonds, based on their relatively high infrared stretching frequencies ( $800-1000\text{ cm}^{-1}$ ) and short bond lengths ( $1.60-1.76\text{ \AA}$ ) [11]. However, the metal-oxygen bond order may be augmented in monoxo complexes of the form  $X_nMO$  (where X = halide or alkoxide and O is a terminal oxo) [12]. Two d orbitals are available to form two  $\pi$ -bonds with the single oxygen, whereas polyoxo complexes have only one d orbital available for  $\pi$ -bonding to each oxygen atom. Thus, monoxo complexes can be considered to possess metal-oxygen triple bonds. One consequence of this phenomenon is that the reactivity of metal oxo groups can be significantly enhanced by the presence of an ancillary (spectator) oxo ligand which drives the reaction by forming a strong triple bond.



This effect implies that the reactivity of surface sites of heterogeneous catalysts should be dependent on the availability of doubly bonded oxo sites. Selective oxidation of propylene and ethanol over supported molybdate catalysts has shown this experimentally [13].

The oxidation of olefins has historically been considered to occur via direct attack of the organic reductant on the oxygen end of a metal oxo moiety [2c], see (i). However, a recent proposal [14], and a theoretical study [12], suggest an alternative mechanism which involves initial nucleophilic attack of the olefin at the metal center forming a  $\pi$ -bound complex, followed by rearrangement to an oxametallacyclobutane intermediate, see (ii). The spectroscopic observation of an osmium oxametallacyclobutane lends support for this suggestion [15].



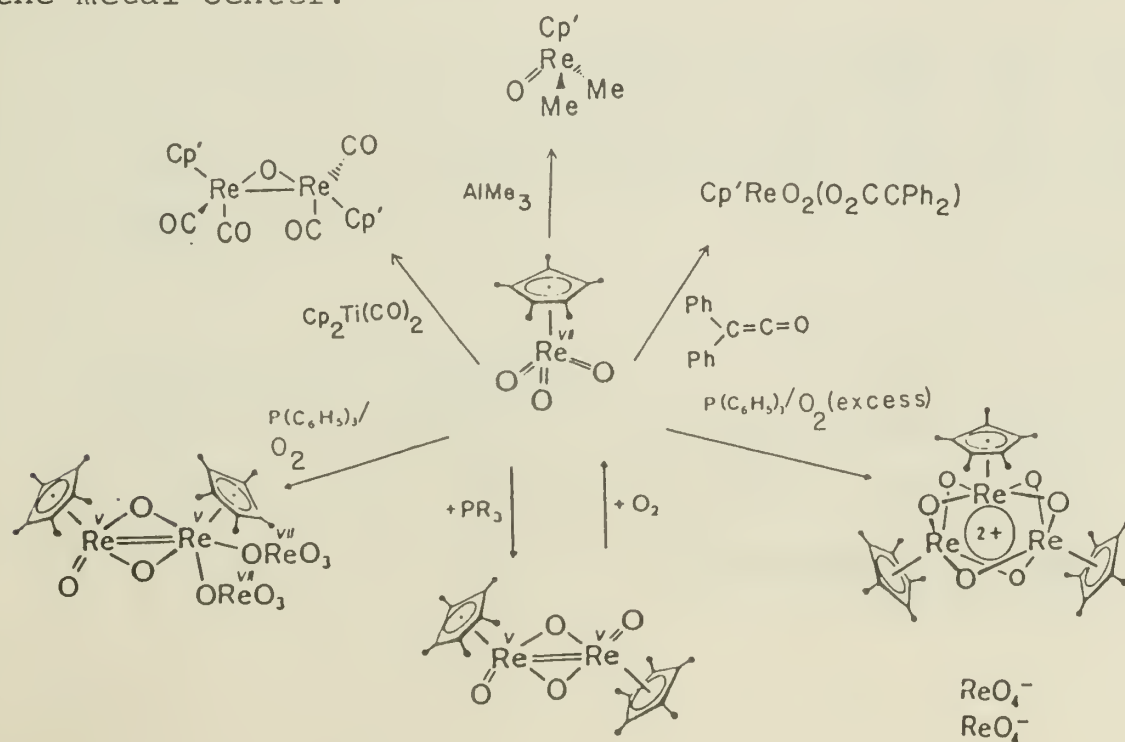


The selective oxidation of propylene to acrolein over supported bismuth molybdate catalysts is proposed to occur via a similar mechanism involving a metal  $\pi$ -allyl complex. Deuterium, carbon-13, and oxygen-18 labeling studies are consistent with this proposal [3,16].

High valent oxo-alkyl complexes are known for V [4], Mo [5], W [6], Re [7-9], and Os [10]. Reactivity studies of these species are, however, limited. The complex  $\text{ReOMe}_4$ , which is formed from the reaction of  $\text{ReOCl}_4$  with methyllithium [7a], does not react with Lewis bases, olefins, alcohols, or mineral acids. It can be oxidized by nitric oxide and dry air to yield the polyoxo compounds  $\text{ReO}_2\text{Me}_3$  and  $\text{ReO}_3\text{Me}$ , respectively. The air stable compound,  $\text{VO}(\text{CH}_2\text{SiMe}_3)_3$ , displays a similar lack of reactivity [4a].

Polyoxo complexes with  $\pi$ -bound cyclopentadienyl ligands form another class of organometallic oxo derivatives. The dimers  $[(\text{C}_5\text{H}_5)\text{MoO}_2]_2$  and  $[(\text{C}_5\text{H}_5)\text{MoO}_2]_2\text{O}$  are unreactive toward olefins, but cleave in the presence of halogens to produce the monomeric oxo halo species  $(\text{C}_5\text{H}_5)\text{MoO}_2\text{X}$  [5a-c]. The Mo(VI) dimer oxidizes triphenyl phosphine and forms a tetramer  $[(\text{C}_5\text{H}_5)\text{MoO}_2]_4$  where each metal is bridged by two oxygens and forms a double bond to a terminal oxygen atom.

The most thoroughly studied organometallic oxo system is that of the half-sandwich Re(VII) complex  $(\text{C}_5\text{Me}_5)\text{ReO}_3$  [9]. This trioxo species is formed by oxidative decarbonylation of  $(\text{C}_5\text{Me}_5)\text{Re}(\text{CO})_3$  under UV irradiation in the presence of oxygen. Lewis acids and Lewis bases induce partial deoxygenation, with concomitant reduction of the metal center.







Although the exact role of organometallic oxo derivatives in selective oxidations is unknown, it is increasingly apparent that complexes containing metal-oxo and metal-carbon bonds are likely intermediates in hydrocarbon oxidation processes.

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The Solid State Ferric Spin-Crossover Transition:  
Spectroscopic, Magnetic, and Structural Investigations

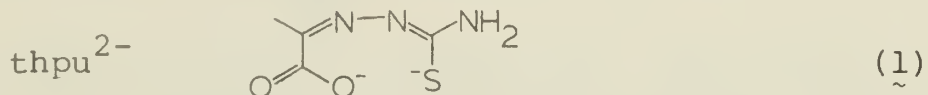
Mark D. Timken

Final Seminar

February 26, 1985

Although most first-row transition metal complexes possess either pure low-spin or high-spin electronic ground states, complexes which show evidence for the thermal population of both spin states are not unknown [1]. These so-called spin-crossover complexes are typically identified by their temperature-dependent magnetic and spectroscopic properties that reflect the changes in the relative populations of the two spin-states. The role of spin-state interconversions in a number of biochemical, oxidation-reduction, and photochemical processes has led to interest in spin-crossover complexes [2]. The research to be reported here has been motivated by two general questions: (1) What factors influence the rates of intramolecular spin-state interconversions? (2) What factors affect the bulk thermodynamics of the solid state spin-crossover transformation? With these questions in mind, three new solid state ferric spin-crossover systems have been synthesized and physically characterized.

Ferric complexes of pyruvic acid thiosemicarbazone (1) have been known for some time to possess spin-crossover properties [3]. As indicated by variable temperature magnetic susceptibility,

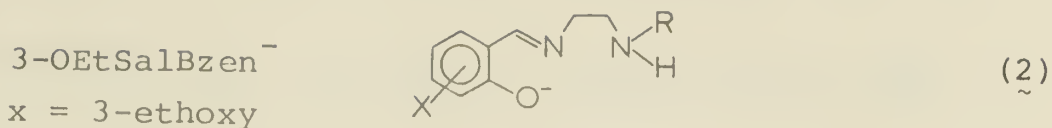


electron paramagnetic resonance, and  $^{57}\text{Fe}$  Mössbauer examinations, the new ferric complex  $[\text{Fe}(\text{Hthpu})(\text{thpu})]$  exhibits a thermally discontinuous spin-state transformation at ca. 230 K. The observation of thermal hysteresis ( $T_c(\uparrow) = 235 \text{ K}$ ,  $T_c(\downarrow) = 225 \text{ K}$ ) identifies the thermodynamic first-order nature of the transition. Distinct and narrow Mössbauer linewidths are evident for both the high- and low-spin electronic states. Two conclusions can be drawn from these observations: (1) the spin-state interconversion rates are slower than  $\sim 10^8 \text{ s}^{-1}$ , (2) short intermolecular Fe-Fe distances are leading to rapid electron spin relaxation times. The chemical inequivalence of the  $\text{Hthpu}^-$  and  $\text{thpu}^{2-}$  ligands has been verified by the single-crystal X-ray structure of  $[\text{Cr}(\text{Hthpu})(\text{thpu})] \cdot \text{H}_2\text{O}$ . Not surprisingly, the chromium complexes are tightly bound in the lattice by a three-dimensional network of hydrogen bonds. Although crystals of the ferric complex were unobtainable, it is likely that similar hydrogen bonding interactions are responsible for the cooperative (i.e., discontinuous) nature of the spin-state transition.

The complex  $[\text{Fe}(3\text{-OEtSalBzen})_2]\text{BPh}_4 \cdot \text{CH}_3\text{CN}(3\text{-OEtSalBzen}^-(2))$  exhibits a very gradual thermal spin-crossover transformation. As seen for similar complexes [4], the observation of distinct high- and low-spin EPR signals suggests that the rate of intramolecular spin-state interconversion is less than  $\sim 10^{10} \text{ s}^{-1}$ .

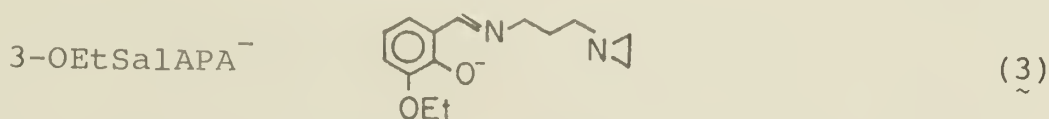






Despite the use of 43% <sup>57</sup>Fe-enriched samples, it is difficult to identify distinct high- and low-spin Mössbauer absorptions due to the very broad linewidths. It is reasonable that the benzyl ligand substituent and the large BPh<sub>4</sub><sup>-</sup> counterions give rise to well separated ferric centers and long spin-spin relaxation times. Consequently, sharp EPR signals are seen, as are magnetically broadened Mössbauer signals.

A number of recent reports [5-8] have shown that ferric complexes with N<sub>4</sub>O<sub>2</sub> ligand atom donor sets can interconvert spin-states rapidly relative to the Mössbauer spectroscopic time scale. Following the work of Federer, the spin-crossover compound [Fe(3-OEtSalAPA)<sub>2</sub>]-ClO<sub>4</sub>·C<sub>6</sub>H<sub>6</sub>(3-OEtSalAPA<sup>-</sup> (3)) has been synthesized and studied in detail. Magnetic and spectroscopic examinations reveal a thermally



gradual and complete spin-crossover transformation. Mössbauer spectroscopy of a 95% <sup>57</sup>Fe-enriched sample shows a single, temperature-dependent quadrupole split doublet; the rate of intramolecular spin-state interconversion is more rapid than ~10<sup>8</sup> s<sup>-1</sup>. Electron paramagnetic resonance studies reveal a spin-state interconversion rate less than ~10<sup>10</sup> s<sup>-1</sup>. Variable temperature (300-13 K) single crystal X-ray diffraction experiments were performed by C. E. Strouse and coworkers at U.C.L.A. These experiments indicate that in addition to the gradual spin-crossover transformation, there is also a first-order (i.e., discontinuous) order-disorder phase transition at ca. 175 K. Although this discontinuous transition does not apparently influence the thermodynamics of the spin-crossover transformation, it is possible that rapid disorder of perchlorate counterions and benzene solvate molecules is coupled to the rapid intramolecular spin-state interconversions.

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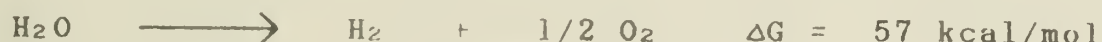
Photochemical Water Splitting: Inorganic  
Dyes as Catalytic Sensitizers.

Edward B. Flint

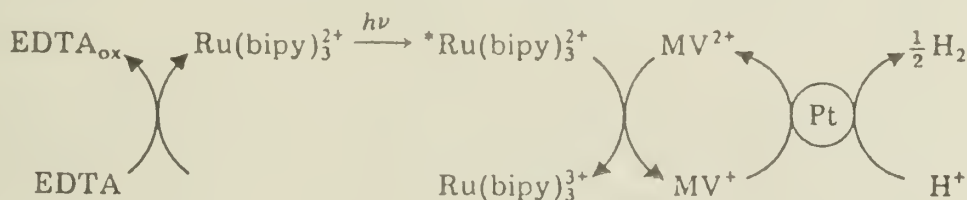
Literature Seminar

March 14, 1985

Since the majority of today's energy demands are met by non-renewable resources, interest in solar energy has been increasing. However, there are many problems associated with sunlight as an energy source. Conversion of visible light into storable energy occurs in plants as photosynthesis, but has proven difficult in artificial systems. Many chemical and physical transformations have been tested as energy storage processes, including semiconductors (solar cells), biomass and chemical reactions.<sup>1</sup> One of the reactions being considered is the splitting of water.



A system that produces  $\text{H}_2$  from water upon irradiation with visible light developed by Moradpour and co-workers<sup>2</sup> as an approach to water splitting is depicted in scheme 1. The



Scheme 1

sensitizer in this system is  $\text{Ru(bpy)}_3^{2+}$  (bpy=2,2'-bipyridine), the excited state of which is capable of reducing methylviologen, ( $\text{MV}^{2+}$ ), to its monocation radical,  $\text{MV}^+$  ( $\text{MV}^{2+}$ =1,1'-dimethyl-4,4'-dipyridinium dication).  $\text{MV}^+$  can react with protons on a colloidal platinum catalyst to produce  $\text{H}_2$ . The exothermic back reaction of  $\text{MV}^+$  and  $\text{Ru(bpy)}_3^{3+}$  is prevented by an excess of EDTA, which rereduces the ruthenium (III) complex. This is an example of a sacrificial system since EDTA is consumed as  $\text{H}_2$  is produced.

This sacrificial system demonstrates some of the important factors to be considered in the design of water splitting systems. The sensitizer should absorb over a significant region of the visible spectrum so as much energy as possible is captured. The lifetime of the excited state should be long enough to allow efficient quenching by the electron relay. The electron relay should be stable in the presence of the catalyst, and the cage escape quantum yield, the ratio of quenching of the sensitizer



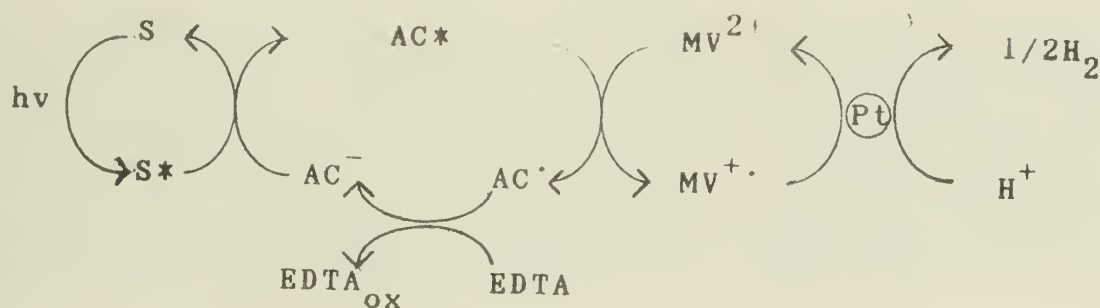


excited state to the rate of production of the reduced electron relay, should be high so as little energy as possible is wasted.

The visible absorbance of  $\text{Ru}(\text{bpy})_3^{2+}$  is adequate, but the excited state lifetime is only on the order of 1 usec<sup>3</sup> at room temperature. This short lifetime dictates that high quencher concentrations be used so production of  $\text{MV}^+$  is efficient.<sup>4</sup> Methylviologen is reduced in the presence of some catalysts,<sup>5</sup> obviously an unwanted side reaction. Finally, the cage escape quantum yield for the  $\text{Ru}(\text{bpy})_3^{3+}/\text{MV}^+$  Couple has been determined to be 0.25,<sup>6</sup> which becomes an upper limit on the efficiency of this system. These considerations have led to the development of new sensitizers, electron transfer agents<sup>7</sup> and catalysts.<sup>8</sup>

The water soluble porphyrin zinc tetrakis(4-methylpyridyl)-porphyrin, ( $\text{ZnTMPyP}^{4+}$ ), has been used as the sensitizer in a similar  $\text{H}_2$  producing system.<sup>9</sup> The yield of  $\text{H}_2$  produced per photon absorbed is improved in this system compared to the ruthenium system for several reasons. The longer lifetime of the excited state, 665 usec vs 1 usec, improves the quenching efficiency, and the improved cage escape efficiency, equal to almost one in this case, means that every absorbed photon results in a reduced  $\text{MV}^+$  in solution. The catalyst used in this study was not the best, so the maximum possible efficiency was not obtained.

Sasse and Mau<sup>10</sup> introduced another modification to this system that improved the yield of  $\text{H}_2$  by increasing the cage escape efficiency. In this case an energy transfer step is added between the excited state sensitizer and the electron carrier, as shown in scheme 2. The 9-anthracenecarboxylate anion, ( $\text{AC}^-$ ), can



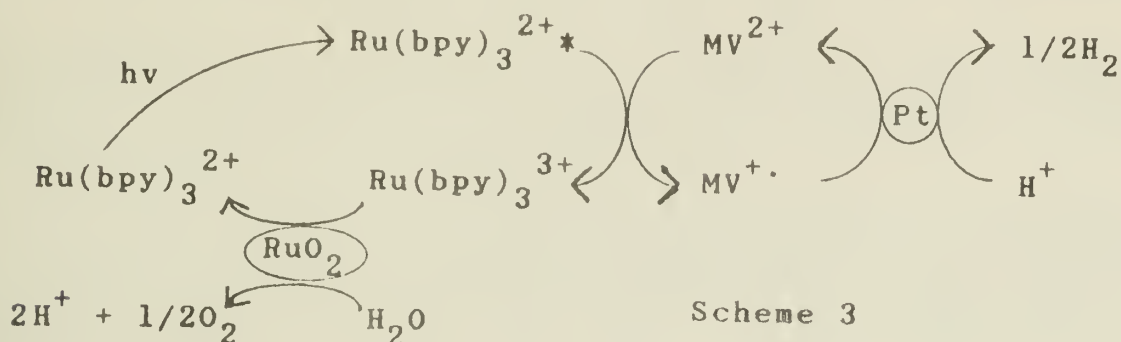
Scheme 2

quench the excited state of  $\text{Ru}(\text{bpy})_3^{2+}$  via energy transfer<sup>11</sup> and then, in the excited state reduce methylviologen. The cage escape yield of  $\text{AC}^-$  approaches one with both the sensitizer and the electron relay. A copper (I) complex  $\text{Cu}(\text{dpp})_2^+$  ( $\text{dpp}$  = 2,9-diphenyl 1,10 phenanthroline)<sup>12</sup> can also be used as the sensitizer in this scheme; it has a much broader absorbance in the visible than  $\text{Ru}(\text{bpy})_3^{2+}$ , which improves efficiency. The major disadvantage of the energy transfer process is its increased complexity: the added components are not stable in the presence of the catalyst.





While these systems are valuable in finding useful components for the reduction of water their limited utility must be kept in mind: sacrificial oxidants are being used irreversibly. Water splitting developed by Gratzel and coworkers<sup>13</sup> which utilizes the technology developed in the sacrificial systems is illustrated in scheme 3. The  $H_2$  is produced in a similar fashion



ion as in the systems described above, but with platinum deposited on colloidal  $TiO_2$  as the catalyst. The  $O_2$  is produced by the reaction of  $Ru(bpy)_3^{3+}$ , the complex after quenching, with water at  $RuO_2$  deposited on colloidal  $TiO_2$ . Since this step is a four electron process it is kinetically limiting, and significant back reaction occurs between  $MV^+$  and  $Ru(bpy)_3^{3+}$ . Hydrogen and oxygen are produced for about 20 hours during continuous irradiation, but production stops due to the competing reaction of  $O_2$  with  $MV^+$  and the degradation of other components. The catalytic components in this scheme are not stable in the presence of the products.

A significant observation about this system is that  $H_2$  and  $O_2$  were produced in the absence of electron relay,<sup>13C</sup> although at reduced yields. The mechanism proposed to explain this involves sensitizer molecules absorbed to the  $TiO_2$  (or within a diffusion radius) that donate electrons directly into the conduction band of the  $TiO_2$ , that was developed to explain the photo-sensitization<sup>14</sup> of electrodes by dyes. This is significant in light of the undesirable reaction of  $O_2$  with  $MV^+$ .

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## Transition Metal Ketenes

Laura M. Babcock

Literature Seminar

March 19, 1985

The mechanism of Fischer-Tropsch catalysis is presently believed to proceed via reactions involving methylene species on metal surfaces [1]. Muettert et al., Herrmann, and Katzer [2] have suggested that carbonyl carbene coupling to form an intermediate ketene complex is one reaction path which could lead to oxygen-containing products. Support for these ketene intermediates arises from the ever increasing number of isolable, transition metal ketene complexes and their subsequent reactivity.

Transition metal ketenes have been observed in several different bonding arrangements. C,O and C,C  $\pi$ -bonding to one or two metal centers have been reported. Terminal, MRC=C=O, and  $\mu_3$  cluster bridged ketene complexes are also known. There are three primary methods for synthesizing transition metal ketenes. Substitution reactions bind a ketene to the metal center by displacement of a weakly bound ligand [3]. Dehydrohalogenation, a general synthetic route to ketene complexes of Zr and Ti, involves proton abstraction from the acyl-halo complex followed by displacement of the halogen by the ketene oxygen [4]. Insertion of a carbonyl into the metal carbon bond of a methylene ligand is, however, the most common method for preparing metal ketenes [5]. CO insertion into other alkylidenes and alkylidyne complexes has been observed as well, Fig. 1. Labeling and reactivity studies on several systems

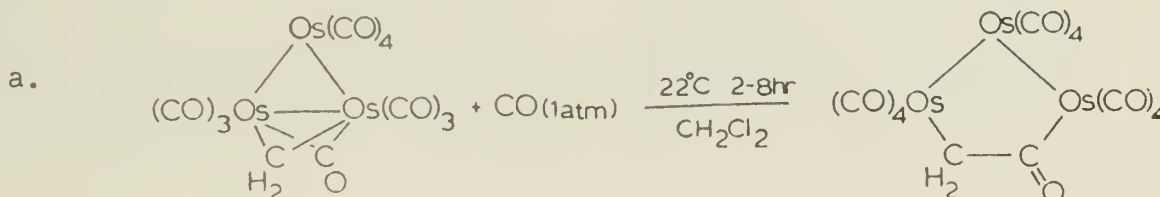
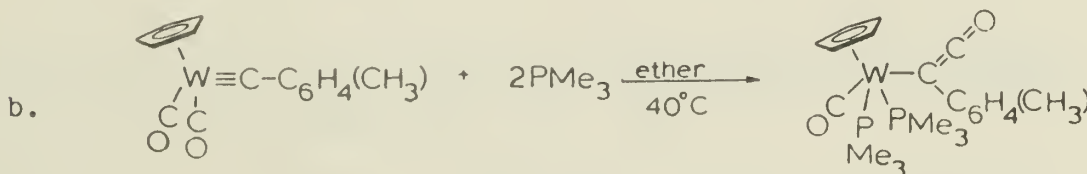


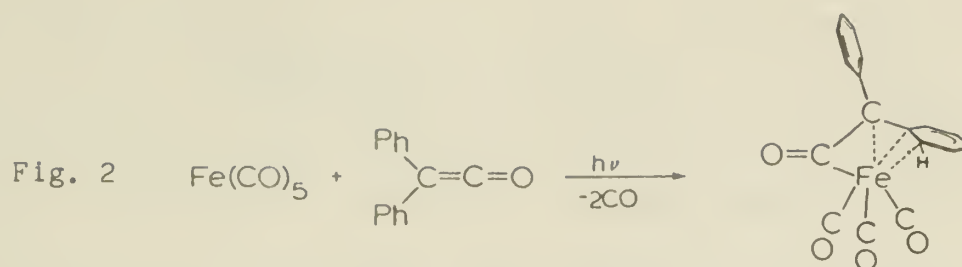
Fig. 1



indicate that both internal carbene-carbonyl coupling [5b,c,6] and insertion of external carbon monoxide [7] are possible pathways for the formation of metal ketenes.

Herrmann has demonstrated that reversible cleavage of the carbon-carbon bond of ketene complexes can occur [8]. Iron pentacarbonyl and diphenylketene were allowed to react in a  $^{13}\text{C}$  enriched CO atmosphere, the resulting  $\sigma$ -acyl,  $\pi$ -allyl complex showed  $^{13}\text{C}$  label incorporation into the metal ketene carbonyl site, Fig. 2. Since labeled carbon monoxide was not incorporated into the free ketene under reaction conditions, these results indicated that





the carbon-carbon bond of the ketene must be reversibly cleaved. When Deeming and Arce [9] reacted ketene with  $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ , they obtained  $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CH}_2)$  which upon heating converted to the ketenylidene species  $\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CCO})$  previously reported by Shapley and coworkers [10]. These cases clearly demonstrate that internal carbene-carbonyl coupling (which results in metal bound ketene complexes) can be a readily reversible process.

Deoxygenation and decarbonylation are common decomposition pathways exhibited by ketene complexes of transition metals [11]. The trinuclear clusters  $\text{H}_2\text{M}_3(\text{CO})_9(\text{CCO})$   $\text{M}=\text{Os}, \text{Ru}$  react with  $\text{H}_2\text{O}$  or  $\text{MeOH}$  to give the corresponding  $\mu_3$ -acid or  $\mu_3$ -ester [10,12]. Similarly, Geoffroy has shown that reaction of  $\text{H}_2\text{O}$  or  $\text{MeOH}$  with the bridging ketene  $\text{Os}_3(\text{CO})_{12}(\eta^2(\text{C},\text{C})\mu\text{-CH}_2\text{CO})$ , Fig. 1a, produces acetic acid or methyl acetate and  $\text{Os}_3(\text{CO})_{12}$  [5c]. Hydrogenation of several ketene systems produces oxygenated hydrocarbons [5c,13]. This reactivity demonstrates that Fischer-Tropsch products can be produced from transition metal bound ketenes, suggesting their involvement in catalytic CO hydrogenation.

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# The Effects of Main Group Atoms on Transition Metal Carbonyl Clusters

Leonard Bogan

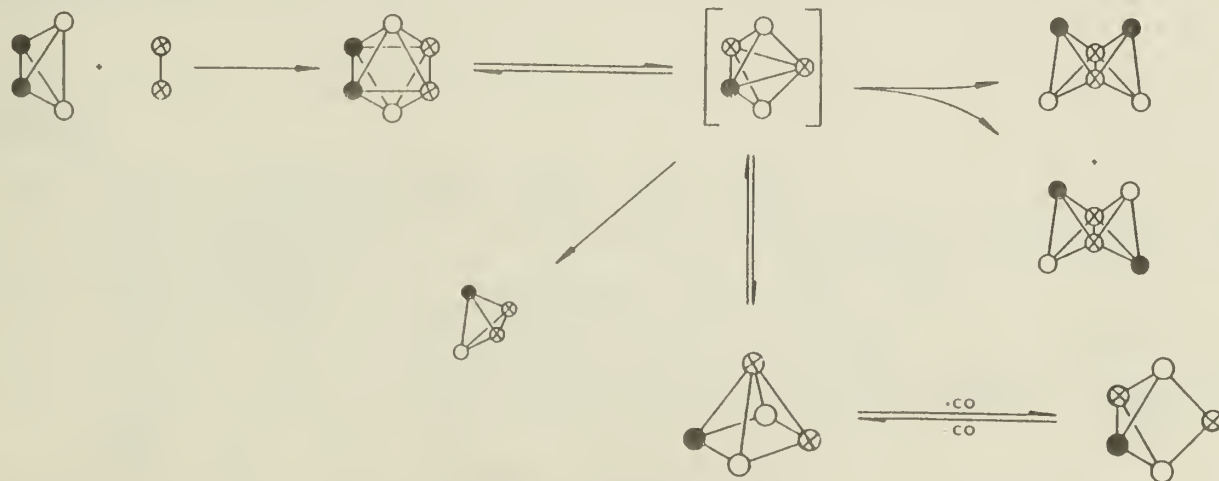
Final Seminar

March 21, 1985

Transition metal carbonyl clusters (TMCCs) have been widely studied as soluble models for metal surfaces in heterogeneous catalysts and as homogeneous catalysts or catalyst precursors themselves [1]. Their rational use in the latter capacity is hampered by their inevitable fragmentation under the conditions of catalysis. Main group elements (MG) have been incorporated into the cluster core to tether the metal atoms together [2], since TM-MG bonds are generally stronger than TM-TM bonds [3]. Sulfur is one of the more commonly used main group elements for this purpose.

Central to control of metal vertex lability in transition metal main group element carbonyl clusters (TMMGCCs) is an understanding of the reaction pathways available to the clusters. Unfortunately, there have been very few such investigations [4]. The study of TMTeCCs is useful to such an understanding for three reasons. First, the chemistry of TMTeCCs complements that of the analogous sulfides; the heavier atom generally stabilizes intermediates which are not observable in TMSCC chemistry. Second, the compounds  $\text{Fe}_3\text{Te}_2(\text{CO})_9$  and  $\text{Co}_4\text{Te}_2(\text{CO})_{10}$  are anomalous in forming adducts with Lewis bases, a reaction the sulfide and selenide analogues do not undergo [4]. Third,  $^{125}\text{Te}$  NMR spectroscopy is a useful probe of the cluster core structure, and as such it complements other methods which probe the ligands on the metal vertexes [5].

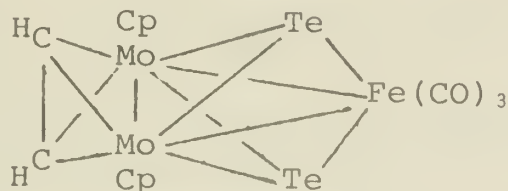
The reaction of  $\text{Fe}_3\text{Te}_2(\text{CO})_9$  with metal carbonyl dimers at 150-180° and under 1300-1750 psi of CO was found to be a convenient route to a variety of TMTeCCs. Comparison of the chemistry of similar Fe-Co-E and Fe-Mo-E (E = S, Te) systems led to the proposal that these reactions proceed by the pathway shown in the scheme below. The novel part of this mechanism is the rearrangement of a  $(\text{TM})_4\text{E}_2$  cluster



by dissociation and recapture of a TM vertex. In the system  $\text{Fe}_2(\text{S}_2)(\text{CO})_6 + \text{Cp}_2\text{Mo}_2(\text{CO})_4$  dissociated  $\text{Fe}(\text{CO})_x$  ( $x < 5$ ) fragments were trapped as  $\text{Fe}_3\text{S}_2(\text{CO})_9$ . The formation of two isomers of  $\text{Cp}_2\text{Mo}_2\text{Fe}_2\text{S}_2(\text{CO})_8$  [6] is explained by this mechanism and a method was devised for isomerization of the cis- isomer to the trans-  $\text{Cp}_2\text{Mo}_2\text{Fe}_2\text{S}_2(\text{CO})_8$ .



Heating  $\text{Cp}_2\text{Mo}_2\text{FeTe}_2(\text{CO})_7$  at  $110^\circ$  generated a reactive intermediate which was trapped with  $\text{Fe}(\text{CO})_5$ ,  $\text{CpCo}(\text{CO})_2$ , and with  $\text{RCCH}$  ( $\text{R} = \text{Ph}, \text{H}$ ). The product of the latter reaction has the formula  $\text{Cp}_2\text{Mo}_2\text{FeTe}_2(\text{CO})_3(\text{RCCH})$ , and its structure was established by a combination of  $^1\text{H}$  and  $^1\text{H}$  coupled  $^{13}\text{C}$  NMR spectroscopy of three different derivatives.



Careful inspection of the crystal structure of  $\text{Cp}_2\text{Mo}_2\text{FeTe}_2(\text{CO})_7$  [7] revealed a short ( $3.14 \text{ \AA}$ )  $\text{Te}\cdots\text{Te}$  contact. Subsequent inspection of the structures of the Lewis base adducts of  $\text{Fe}_3\text{Te}_2(\text{CO})_9$  and  $\text{Co}_4\text{Te}_2(\text{CO})_{10}$  revealed similar short  $\text{Te}\cdots\text{Te}$  distances in those compounds. It is proposed that the anomalous Lewis acidity of  $\text{Fe}_3\text{Te}_2(\text{CO})_9$  and  $\text{Co}_4\text{Te}_2(\text{CO})_{10}$  is due to the stabilizing effect of those  $\text{Te}\cdots\text{Te}$  interactions.

The two electron reduction of  $\text{Fe}_3\text{Te}_2(\text{CO})_9$  was found to be reversible, but attempts to isolate the stable dianion and compare its structure with that of the isoelectronic adduct  $\text{Fe}_3\text{Te}_2(\text{CO})_9(\text{PPh}_3)$  failed. Oxidation of  $\text{Cp}_2\text{Mo}_2\text{FeTe}_2(\text{CO})_7$  (which is isoelectronic with  $\text{Fe}_3\text{Te}_2(\text{CO})_9\text{L}$  and has a similar structure) with  $\text{Br}_2/\text{CO}$  gave a good yield of  $\text{CpMoFe}(\text{Te}_2\text{Br})(\text{CO})_5$ , which features a novel  $\text{Te}_2\text{Br}$  ligand. In solution the compound undergoes rapid exchange of Br making the Te atoms equivalent, but at  $-88^\circ$  in toluene this exchange is slowed enough that  $^1\text{H}$  NMR indicates a chiral compound.

Reaction of  $\text{AgSbF}_6$  with  $\text{CpMoFe}(\text{Te}_2\text{Br})(\text{CO})_5$  generates the cation  $[\text{CpMoFe}(\text{Te}_2)(\text{CO})_5]^+$ . This compound reacts with a variety of nucleophiles to give products resulting from initial attack at Te. This behavior is novel in that the main group element is more reactive than the transition metals.

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# Synthetic Metals: Structural Control of Electronic Properties

Kira M. Glover

March 26, 1985

A variety of molecular systems in the solid state exhibit the electrical, optical and magnetic properties of metals. Three systems of particular interest to the inorganic chemist are: (1) partially oxidized platinum complexes; (2) metallomacrocycles; and (3) chalcogen network compounds. These systems can be chemically modified in terms of structure, degree of partial oxidation (DPO), counterions, etc., and the effects of these modifications on physical properties lead to a clearer understanding of the metallic state. Other goals of synthetic metal synthesis include retention of metallic behavior at low temperatures and room temperature superconductivity [1,2].

Among the first synthetic metals were stacked  $\text{Pt}(\text{CN})_4^{2-}$  units, forming a large family of partially oxidized tetracyanoplatinate salts (POTCP) initially derived from  $\text{K}_2[\text{Pt}(\text{CN})_4]\text{Br}_{0.30} \cdot 3\text{H}_2\text{O}$ , Krogmann's salt  $[\text{KCP}(\text{Br})]$  [3]. The POTCP salts were followed by tetrathiafulvalene-tetracyanoquinone (TTF-TCNQ) [4], the first highly conducting ( $\sigma_{\text{RT}} \approx 200 \Omega^{-1}\text{cm}^{-1}$ ) organic solid. These two systems typify synthetic metals. They consist of closely spaced planar units forming segregated stacks in which intermolecular orbital overlap gives rise to energy bands along the stacking axis. As conduction can then easily occur only along the stacking axis, these compounds exhibit highly anisotropic conductivities;  $\sigma_{\parallel}/\sigma_{\perp}$  can be as high as  $10^5$  [5].

Due to this quasi-one-dimensionality, these compounds are electronically unstable with respect to a variety of one-dimensional to three-dimensional transitions. The Peierls distortion [6] refers to a permanent periodic lattice distortion that opens up a gap in the energy band structure. X-ray diffraction is then clearly a powerful tool in observing Peierls transitions. This phase transition is similar to the Jahn-Teller distortion in molecules in that filled electron states are lowered in energy and unfilled states raised.

The effect of structural changes on conductivity has been studied in seventeen well-characterized POTCP salts,  $\text{M}_x[\text{Pt}(\text{CN})_4]\text{X}_y \cdot n\text{H}_2\text{O}$ , which form a family of compounds with varying Pt-Pt distances ( $d_{\text{Pt-Pt}}$ ) [5,9-12]. All of these compounds exhibit modulated structures due to Peierls distortions. The complexes vary with regard to DPO, Peierls band gap ( $\Delta$ ), three-dimensional ordering temperature ( $T_{3D}$ ) and the theoretically derived interchain coupling ( $\eta$ ) and electron-phonon coupling ( $\lambda$ ) parameters. All of these parameters can be correlated with  $d_{\text{Pt-Pt}}$ , and the correlations can be understood in terms of changes in the energy band structure with varying Pt-Pt distances.

The metallomacrocycles [14-17], studied primarily by Marks, Hoffman, and Ibers, form another chemically variable system. The best understood system is the phthalocyanines (Pc). Nickel phthalocyanine [18],  $[\text{NiC}_{32}\text{H}_{16}\text{N}_8]$ ,  $\text{Ni}(\text{Pc})$ , crystallizes in a stacked structure of planar rings, which when oxidized by iodine, becomes a synthetic metal ( $\sigma_{\text{RT}} = 500 \Omega^{-1}\text{cm}^{-1}$ ).  $\text{Ni}(\text{Pc})\text{I}$  exhibits metallic properties to below 2 K; this absence of any metal-insulator transition is due to



the presence of disordered  $I_3^-$  chains and the lack of significant interstack interactions. As Ni(Pc) charge-transfer complexes proved to be integrated stack insulators, attempts to control stacking architecture resulted in the synthesis of cofacially-linked Pc polymers,  $[M(Pc)O]_n$  [19,20]. Variation of the ring center species, M, leads to variation of the Pc-Pc interplanar spacing ( $d_{Pc-Pc}$ ). Increasing  $d_{Pc-Pc}$  (Ni < Si < Ge) decreases the conductivity, increases the Pauli-like magnetic susceptibility( $\chi$ ) and decreases the optical reflectivity frequency ( $\omega$ ), all indicating a structurally correlated decrease in bandwidth.

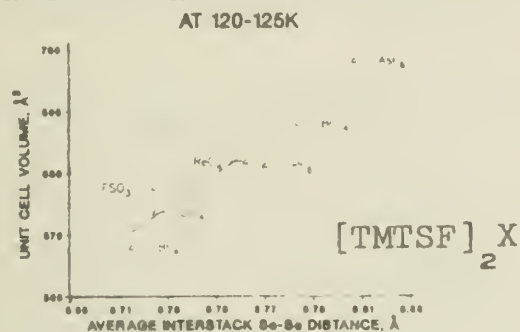


Figure 1

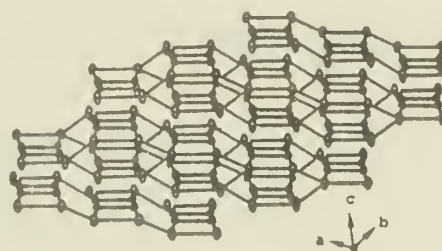


Figure 2

The discovery of pressure-induced superconductivity in  $(TMTSF)_2PF_6$  [21] ( $TMTSF$  = tetramethyltetraselenofulvalene) led to a variety of  $(TMTSF)_2X$  [22,22] compounds, culminating in  $(TMTSF)_2ClO_4$  [24], an ambient-pressure superconductor with  $T_C = 1.1$  K. The structures of these  $(TMTSF)_2X$  salts indicate formation of a three-dimensional network [25] of selenium atoms, the TMTSF conduction pathway. Recent x-ray diffraction studies produced a correlation between anion size and Se-Se distances [26] ( $d_{Se-Se}$ ) with minimum  $d_{Se-Se}$  centering around  $(TMTSF)_2ClO_4$  (Figure 1). From this correlation, unit cell volume and thus, Se-Se distances, can be predicted from anionic size. Two other ambient pressure superconductors are based on BEDT-TTF [23, 25,27] (bisethylenedithiolotetrathiafulvalene):  $(BEDT-TTF)I_3$  [28] and  $(BEDT-TTF)IBr_2$  [29]. Unexpectedly the S-S intrastack interactions are significantly weaker than the interstack interactions leading to formation of an infinite two-dimensional sulfur atom network (Figure 2). Changing the  $I_3^-$  anion to the shorter ( $\sim 7\%$ )  $IBr_2^-$  anion, results in a contraction of the S-S network and an increase in the superconductivity onset temperature ( $T_C$ ), from 1.4 K to 2.7 K. Such chalcogen network superconductors are very different from the majority of synthetic metals as they are not one-dimensional. Hopes to further raise  $T_C$  center on tellurium-based compounds

Clearly, from a synthetic chemical standpoint, the ability to tailor charge-transporting microstructures at the atomic level represents both an exciting challenge and a key to manipulating macroscopic properties and to testing theoretical predications. In the future, new synthetic systems will lead to a greater understanding of the complex interrelationships between structure and electronic properties.

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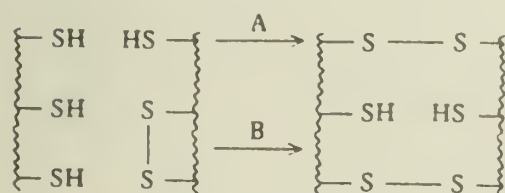


# Anti-arthritis Gold Drugs: A Bioinorganic Approach

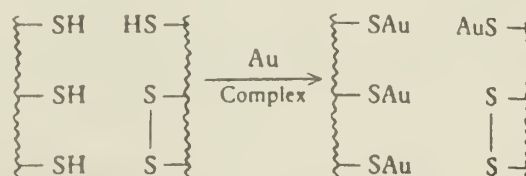
Mary Mills

March 28, 1985

Chrysotherapy, the use of gold complexes in the treatment of rheumatoid arthritis (R.A.), originated in the work of the French physician, Jacques Forestier, who reported on the anti-inflammatory effect of gold thiopropanol sodium sulfonate in 1929. Since that time additional gold-containing compounds have been found effective in treating R.A., but as yet no mechanism of action has been firmly established. Proposed modes of action [1] for the gold drugs rely on the great affinity of gold for sulfur ligands and on its preference for a two-coordinate linear geometry. As one possibility, it is suggested that gold binds to reduced thiol functionalities (cysteine residues) in the affected joint and thereby protects certain critical thiol groups from oxidation via inter- or intramolecular disulfide bond formation [2].

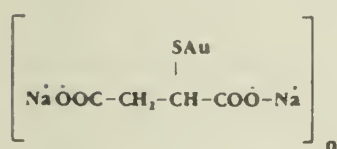


Protein thiol oxidation and  
disulfide interchange

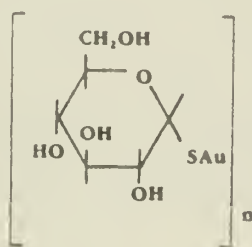


Thiol blockage by gold complex

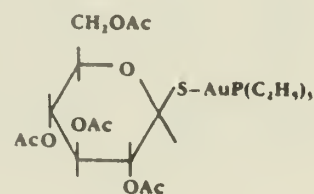
The two most commonly used gold drugs in the U. S. are sodium gold(I) thiomalate (1) and gold(I) thioglucose (2) shown below.



1



2



3

Another gold(I) complex, (2,3,4,6-tetra-O-acetyl-1-thio- $\beta$ -D-glucopyranosato-S-(triethylphosphine)gold(I) (generic name auranofin, 3), shows potent anti-arthritis activity and has several advantages compared to the gold(I) thiolates. One of these is the ability of auranofin to be administered orally rather than through intra-muscular injection [3].



The electronic configuration of gold(I) is  $d^{10}$ , making traditional spectroscopic techniques such as electronic paramagnetic resonance and ultraviolet-visible spectroscopy uninformative. However, improvements in nuclear magnetic resonance (nmr) [4] and  $^{197}\text{Au}$  Mössbauer spectroscopy [5] have made these techniques very useful for in vitro and in vivo studies. More recently, both Extended X-Ray Absorption Fine Structure (EXAFS) and X-Ray Absorption Near Edge Structure Spectroscopy (XANES), have also been used with considerable success [6]. The use of these techniques to probe gold-containing complexes in biological systems requires thorough initial in vitro studies in which relevant model complexes are characterized. These studies reveal trends and spectral patterns which are enormously useful once in vivo investigations have begun.

Model studies based on  $^{197}\text{Au}$  Mössbauer Spectroscopy have utilized the well-established linear relationship between isomer shift and quadrupole splitting to determine not only gold oxidation state and coordination number, but the nature of the coordinating ligands as well [7]. Similarly, x-ray absorption spectroscopy yields information about the number and kinds of ligands around the gold atom as well as its oxidation state. The results obtained are quite accurate due to the presence of unusual spectral features in both the edge and EXAFS regions [8].

With model studies serving as a foundation, in vivo investigations may be undertaken. Most of these studies have concentrated on drug interactions with a few known biological target molecules, among them, serum albumin (SA), glutathione (GSH), and metallothionein (MT). These very different molecules are attractive binding sites for gold because each has at least one reduced thiol group, with which the gold drug is thought to interact. Interaction of gold(I) drugs with GSH and SA seems to occur via ligand exchange reactions, thus allowing the gold atom to remain two coordinate [9]. XAS and nmr studies on auranofin reveal that the complex binds to the protein thiol group with concomitant loss of its thioacetylglucose ligand [10]. This result is expected, considering the excellent trans-labelizing nature of phosphines. The behavior seen for the gold(I) thiol complexes (1 and 2) also seems to involve ligand exchange reactions [11].

Further interesting results come from isolation and examination of cell bodies called lysosomes following administration of 1 or 3. These lysosomes, termed aurosomes, accumulate very high concentrations of gold within 18 hours after administration of the gold drug. Most intriguing is the fact that by XAS the gold environments in aurosomes treated with 1 and 3 are identical, indicating ligation to two sulfur atoms [8]. This result suggests that the gold-phosphine bond has been broken, raising new questions about the active forms of these drugs.



These limited bioinorganic experiments still leave unanswered some of the important questions concerning the medically active form of gold drugs and the importance of the gold atom in drug activity. Future work in this area will benefit greatly from improvements in the spectroscopic probes applicable to the study of gold-containing systems.

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## Redox Chemistry of Aqueous Molybdenum

Kenneth M. Rahmoeller

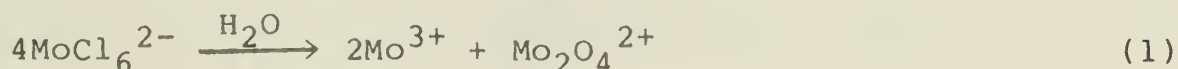
Final Seminar

August 14, 1985

The redox chemistry of aqueous molybdenum ions is fairly complicated and has required over 30 years of work to reach the present state of knowledge.[1] Among the many reasons for this complexity are the existence of several different structural forms for some of the oxidation states,[2] the great tendency for molybdenum to disproportionate and conproportionate to produce secondary products,[3] and the lack of experimental techniques for characterizing the resulting products. Although the redox reactions of molybdenum in the oxidation states of +6 to +2 are now considered "known", a review of these redox studies reveals the widespread use of large excesses of the oxidizing/reducing agent with respect to the molybdenum species being studied.[4] In these cases, it is usually not possible to determine whether the observed product was the initial product or the result of secondary reactions with the excess oxidant/reductant.

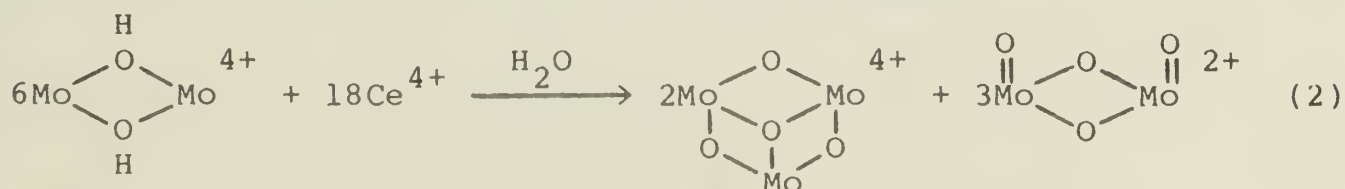
In an attempt to reinvestigate these systems, potentiometric titrations of the various molybdenum species by the appropriate oxidant/reductant were performed. In this way, not only were excesses of the redox agent avoided, but also the progress of any reaction could be monitored by the observed potential at a gold or platinum electrode.

In initial studies, the oxidation of  $\text{Mo}^{3+}$  by all oxidants ( $\text{Ce}^{4+}$ ,  $\text{Mo(VI)}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , etc.) resulted in the sole production of  $\text{Mo}_2\text{O}_4^{2+}$ , the only known stable form of  $\text{Mo(V)}$  and the expected product as suggested by the literature.[5] No indication of  $\text{Mo(IV)}$  was found, despite the use of  $\text{Ce}^{4+}$  as a one electron oxidant. Subsequent studies with  $\text{Mo(IV)}$  halides ( $\text{MoCl}_4$ ,  $(\text{Et}_4\text{N})_2\text{MoCl}_6$ , etc.) demonstrated that rapid disproportionations occurred upon their contact with water,



thus showing the instability of monomeric  $\text{Mo(IV)}_{\text{aq}}$  and explaining its absence as a product during the oxidation of  $\text{Mo}^{3+}$ .

Contrary to the literature,[6] the oxidation of  $\text{Mo}_2(\text{OH})_2^{4+}$  yields equal amounts of  $\text{Mo(IV)}$  and  $\text{Mo(V)}$ .



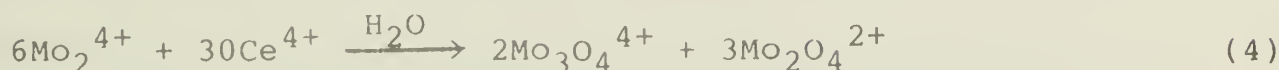
Reaction 2 occurs under all conditions and is oxidant independent. Although the use of  $\text{Mo(VI)}$  as oxidant introduces another source of molybdenum, the resulting products remain the same.



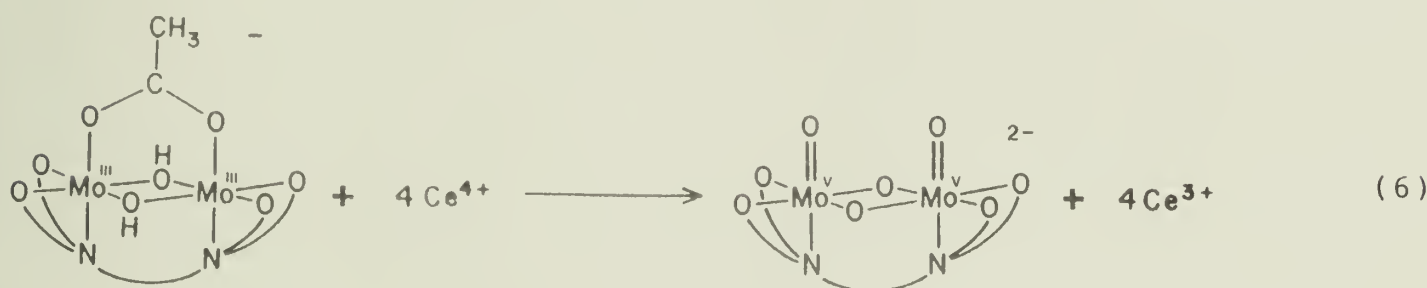
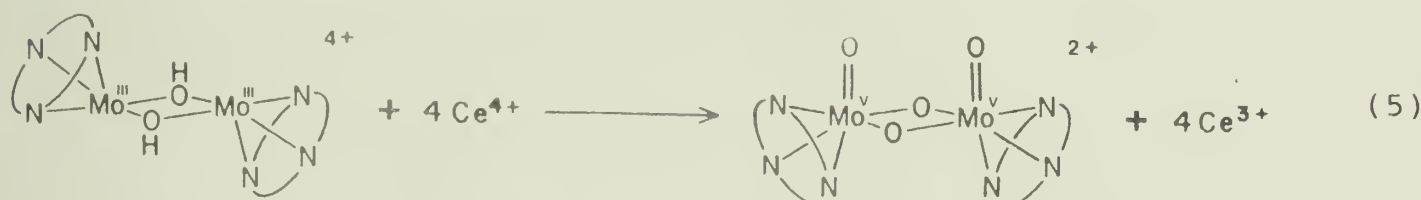


$^{95}\text{Mo}$  labeling studies show that molybdenum from both reactants are found in both products in approximately a 1:1 ratio.

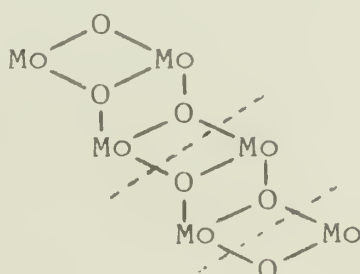
A similar reaction occurs with dimeric  $\text{Mo}_2^{4+}$ .



A common intermediate (or activated state) is suspected for these reactions. The intermediate is probably a large (4 or more molybdenum atoms) molybdenum-oxygen oligomer produced by the combination of two or more molybdenum dimers resulting from the initial oxidation of  $\text{Mo}_2(\text{OH})_2^{4+}$  or  $\text{Mo}_2^{4+}$ . Removal of coordination sites from the original molybdenum starting materials with chelating agents changes the product stoichiometries, probably by inhibiting the formation of large oligomeric intermediates.



Large oligomeric intermediates would allow the necessary trimeric and dimeric structures found in the products to be pre-formed with very few rearrangements. For example:





Oxidation of  $\text{Mo}_4\text{O}_4(\text{OH})_2^{4+}$  and  $\text{Mo}_4\text{O}_6^{4+}$  give the same  $2\text{Mo}_3\text{O}_4^{4+}/3\text{Mo}_2\text{O}_4^{2+}$  ratio suggesting their close similarity to the proposed intermediate.

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## Borazines and Their Transition Metal Complexes

Stanley N. Milam

Literature Seminar

November 14, 1985

Borazine and alkyl substituted borazines are six membered planar heterocyclic rings of three nitrogen and three boron atoms in alternation; they are isoelectronic and isostructural analogs of benzene and alkyl benzenes.

The synthesis of borazine,  $H_3B_3N_3H_3$ , from  $B_2H_6 \cdot 2NH_3$  was first reported by Alfred Stock in 1926 [1]. A more convenient synthetic approach from boron trichloride and ammonium or alkylammonium halides results in formation of B-trichloroborazine or B-trichloro-N-trialkylborazine, respectively [2]. The synthesis of borazines from sodium borohydride and ammonium halides has also been demonstrated [3]. Symmetric B-trialkylborazines may be prepared by reaction of B-trichloroborazine with an appropriate alkali-metal-alkyl or Grignard reagent [4]; asymmetric B-alkylborazines may be prepared similarly [5]. Asymmetric N-alkylborazines are prepared by reaction of mixtures of ammonium and alkylammonium halides with boron trichloride or alkali-metal borohydrides [6]. Another route to asymmetric N-alkylborazines is by reaction of methyl lithium with B-trialkylborazine followed by addition of alkyl halide to yield N-monoalkyl-, N-dialkyl-, and N-trialkyl-B-trialkylborazines [7].

A battery of physical measurements have been performed on several borazines to determine if any similarities to arenes exist. Electron diffraction analyses of borazines have shown that the B-N bond is shorter than a B-N single bond [8]. Calorimetric studies indicate that the boron nitrogen bond energy is a function of substituents on both boron and nitrogen [9]. The boron-11 NMR shift is related to the donor ability of substituents on the boron atoms [10,11]. The nitrogen lone pairs on the borazine appear to be delocalized to boron; the extent of delocalization is dependent on the nature and location of the ring substituents.

In an attempt to find organic chemistry analogous to that of arene metal tricarbonyl complexes, borazine metal tricarbonyl complexes of chromium, molybdenum, and tungsten have been prepared and investigated. The borazine complexes are made from  $fac-(H_3CCN)_3M(CO)_3$  or photolytically from  $M(CO)_6$  [12,13].

The X-ray structure of hexaethylborazine chromium tricarbonyl is a piano stool molecule with a puckered ring [14]. The carbonyl infrared stretching frequencies of several borazine metal complexes suggest that borazines and arenes cause comparable electronic perturbations of the chromium tricarbonyl moiety [15]. The metal to ligand charge transfer band of borazine chromium tricarbonyl complexes occurs at lower energy than for the analogous arene molecule suggesting that borazines are better acceptor ligands than arenes [16].

The wealth of organic chemistry demonstrated to occur on the ring of arene chromium tricarbonyl complexes is not observed for analogous borazine complexes. Borazines are easily displaced from metal tricarbonyl complexes by basic metal anions, e.g.  $SnCl_3^-$ , and by neutral sigma donors, e.g. phosphites to yield free borazine and  $L_3M(CO)_3$  [16,17,18].



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## Ti, V, Nb Metalloporphyrin Chemistry

Jong-Hee Hwang

Literature Seminar

November 21, 1985

In recent years, much interest has been shown in synthetic analogs of various biological systems. The bioinorganic approach to the understanding and utilizing of hemoproteins has led to numerous studies of synthesis and reactivity of dioxygen adduct of metal complexes. Relatively few studies of Ti, V, Nb porphyrins have been published [1-20], however, Nb, V and Ti show appropriate characteristics for the study of  $O_2$  binding [1].

The first peroxoporphyrin metal complex with symmetrically bonded dioxygen was reported in 1976 [2]. The dihalide complexes, which are precursors of low valent titanium complexes which will bind dioxygen, were prepared in 1977 [3-6]. Low valent titanium complexes show various types of autoxidation, which are determined by characteristics of axial ligands [7,8,10]. Recently, it was reported that titanium porphyrin compounds are catalysts for the epoxidation of olefins by alkylperoxides [9].

In 1934, the first oxovanadium(IV) porphyrin complex was found in petroleum and shale. However, the inertness of  $V=O$  moiety limited the study of vanadium porphyrin chemistry. Low valent vanadium(II) can be prepared from vanadium(IV) porphyrin halides [11,12], but vanadium(III) complexes have not been reported yet.

A French group succeeded in the preparation of acetato-oxo niobium(V) and trioxo niobium(V) complexes [13]. The crystal structures of these complexes were determined, and the complexes were found to be seven-coordinate [14-16]. The porphyrin complex of a tri- $\mu$ -oxo niobium dimer ( $Nb_2TPP_2O_3$ ) has two different structures from different solvents, which means that the complex ( $Nb_2TPP_2O_3$ ) has several stable configurations, depending on the nature of the crystallization solvent. Niobium(IV) porphyrin complexes of  $O_2$  have been reported [18]. Using the  $O_2$  complex, catalytic activity of niobium porphyrins for photochemical induced epoxidation was reported in 1985 [19].

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## The Chemistry of Triruthenium Hydrocarbyls

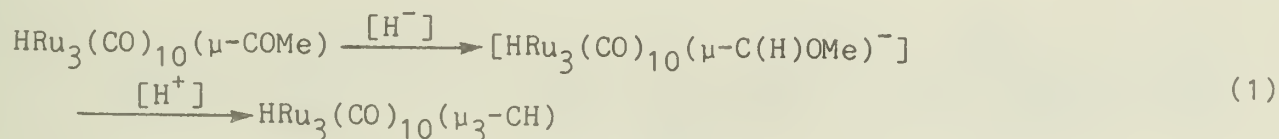
Jennifer S. Holmgren

Final Seminar

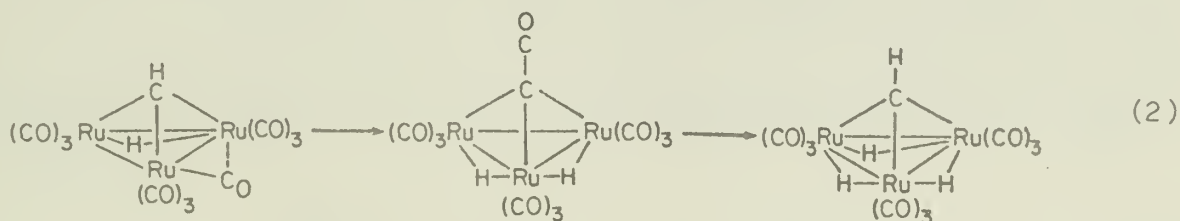
December 11, 1985

Scientists seeking to improve the reactivity and selectivity of CO-hydrogenolysis catalysts may benefit from an improved mechanistic understanding of surface processes. The complexity of these catalytic processes and the difficulties inherent in examining surface reactions, however, has forced researchers to study polynuclear transition metal compounds. Such compounds feature adjacent metal sites and hence serve as useful models for metal surfaces [1]. Recent studies have focused on the synthesis and characterization of key ligand types including cluster-bound alkyl, alkylidene and alkylidyne groups [2]. We have sought an improved understanding of the interconversion and coupling of such ligands through the use of labile triruthenium hydrocarbyl clusters.

The methoxy-substituted carbyne cluster,  $\text{HRu}_3(\text{CO})_{10}(\mu\text{-COCH}_3)$  [3], provides a readily accessible route to the triruthenium methylidyne cluster,  $\text{HRu}_3(\text{CO})_{10}(\mu_3\text{-CH})$  (reaction 1) [4].



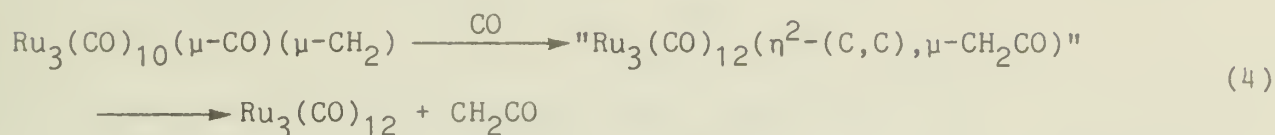
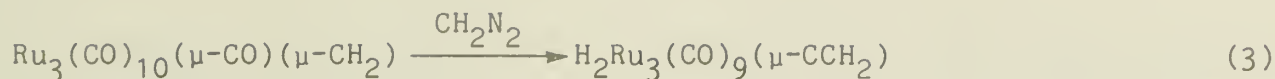
Variable temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments suggest the intermediacy of a formyl complex, presumably  $[\text{HRu}_3(\text{CO})_9(\text{C(H)O})(\mu\text{-COCH}_3)^-]$ , in the preparation of  $\text{HRu}_3(\text{CO})_{10}(\mu_3\text{-CH})$ . The methylidyne cluster,  $\text{HRu}_3(\text{CO})_{10}(\mu_3\text{-CH})$ , rearranges rapidly ( $-10^\circ\text{C}$ ) to the isomeric carbonylmethylidyne cluster,  $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CCO})$ , via intramolecular coupling of the carbyne ligand and a cluster-bound carbonyl. Hydrogenation of  $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CCO})$  yields  $\text{H}_3\text{Ru}_3(\text{CO})_9(\mu_3\text{-CH})$  [3], demonstrating that this C-C coupling process is reversible (reaction 2)



The carbonylmethylidyne cluster,  $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CCO})$ , is reduced to the vinylidene cluster,  $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu\text{-CCH}_2)$  [5], with  $\text{BH}_3\cdot\text{THF}$ . This reduction is particularly noteworthy as it points to the possibility of isolating hydrocarbons, not just oxygenated products, from chain growth processes involving intact CO.

The triruthenium methylene cluster,  $\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CH}_2)$ , is prepared by the reaction of diazomethane and  $\text{Ru}_3(\text{CO})_{12}$  [6]. Reactivity studies point to facile C-C bond formation involving the cluster bound methylene and added diazomethane or added CO (reactions 3 and 4). The methylene cluster,  $\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CH}_2)$ , thermally rearranges to the carbonylmethylidyne cluster,  $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CCO})$ . This rearrangement probably involves the previously discussed methylidyne cluster,  $\text{HRu}_3(\text{CO})_{10}(\mu_3\text{-CH})$ .



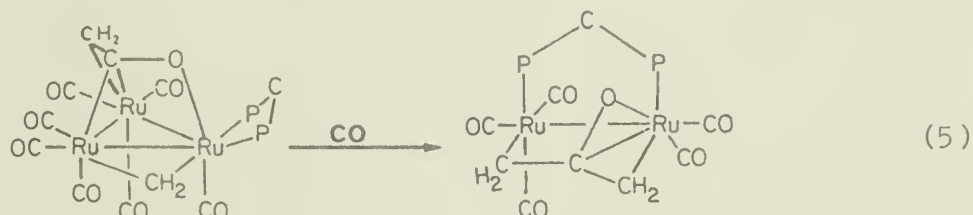


The mobility of surface-bound ligands has received a great deal of attention in recent years due to the proposed importance of such rearrangements to catalytic processes [7]. Spin saturation transfer experiments on  $\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CH}_2)$  suggest that the methylene unit can move over the cluster face, presumably via a bridge-to-terminal isomerization process (Scheme 1). This is the first example supporting such an isomerization process for a cluster bound alkylidene ligand.

Scheme 1



Reaction of diazomethane with the phosphine substituted triruthenium cluster,  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  [8], yields the novel cluster,  $\text{Ru}_3(\text{CO})_7(\eta^3\text{-(C,C,O)}, \mu_3\text{-COCH}_2)(\mu\text{-CH}_2)(\text{dppm})$  [9]. This cluster was characterized spectroscopically as well as by a single crystal X-ray diffraction study. The cluster contains a ketene ligand and a bridging methylene ligand. Surprisingly, each of the three atoms in the C-C-O unit, the ketene ligand, is bound to a different metal atom in the cluster. On addition of CO, the ketene and methylene ligands in  $\text{Ru}_3(\text{CO})_7(\eta^3\text{-(C,C,O)}, \mu_3\text{-COCH}_2)(\mu\text{-CH}_2)(\text{dppm})$  couple to form an oxoallyl unit while the triruthenium cluster degrades to a ruthenium dimer,  $\text{Ru}_2(\text{CO})_5(\eta^4\text{-(C,C,C,O)}, \mu\text{-CH}_2\text{C(O)CH}_2)(\text{dppm})$  (reaction 5), which was characterized by single crystal X-ray diffraction.





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Mössbauer and Structural Studies:  
Characterization of Mixed-Valence Biferrocenes and Iron-Semiquinone Complexes

Michelle Cohn

Final Seminar

December 12, 1985

Mixed-valence and spin-coupled systems owe their seeming ubiquity in biological reaction centers and molecular metals (both conducting and magnetic) to their ability to undergo electron transfer and magnetic exchange processes, respectively. In order to understand the fundamental nature of these processes and ultimately, to design molecules which utilize these processes in attaining desired properties, the determination of the electronic structure of these systems and related inorganic and organometallic compounds has been of continuing interest [1-3].

Mössbauer spectroscopy both with and without an applied magnetic field was found to be useful in characterizing the electronic ground state for a number of mixed-valence biferrocene-type compounds and iron complexes with o-quinone derived ligands. Possible pathways for electron transfer and magnetic exchange interactions were indicated by determining the amount of unpaired spin actually at the iron sites in these compounds.

The magnetic hyperfine properties of four spin-coupled o-semiquinone ( $S=1/2$ ) complexes were studied with high magnetic field Mössbauer spectroscopy and compared to a closely related high-spin ferric ( $S=5/2$ ) complex. The number of unpaired electrons found from magnetic susceptibility studies correlates linearly with the hyperfine interaction, while the magnitude and sign indicates a primarily Fermi-contact interaction. By using a vector coupling approach to find the hyperfine interaction at the component high-spin ferric ion of each exchange coupled unit, good agreement was found between these values and that of the related high spin ferric complex in this study and others in similar environments. These compounds appear to be best formulated as having high-spin ferric ions strongly coupled with semiquinone ligands and having little or no covalency.

The small internal field found at the iron(III) ion in the mixed-valence biferrocenium cation was found to be a result of spin-relaxation effects rather than the "unpaired electron resides in an orbital of predominantly ligand character" as previously suggested [4]. The effective magnetic field at a number of ferrocenium salts (which relaxed at rates either slow, intermediate, or fast with respect to the Larmor precession frequency) and at several other biferrocenium cations (both localized and delocalized with respect to the zero-field Mössbauer timescale) was measured as a function of temperature and applied magnetic field. Two biferrocenium salts apparently unaffected by relaxation were simulated with an  $S=1/2$  spin Hamiltonian. In all cases the unpaired electron appeared to reside in a highly anisotropic orbital characteristic of a low-spin ferric ion [5].

The intramolecular electron transfer characteristics of biferrocenium triiodide were studied by variable-temperature Mössbauer spectroscopy. A sample history dependence of the electron transfer properties was found indicating intermolecular control of this intramolecular process [6]. A determination of the factors involved was attempted by a comparison of the single-crystal X-ray diffraction study [7] with powder X-ray diffraction measurements, and also by





obtaining differential scanning calorimetry measurements on the phase transition seen for this compound. Single crystal conductivity measurements gave low conductivity values and a linear  $\log(\sigma)$  vs  $1/T$  plot, indicating that intermolecular electron transfer processes were at most minimally involved.

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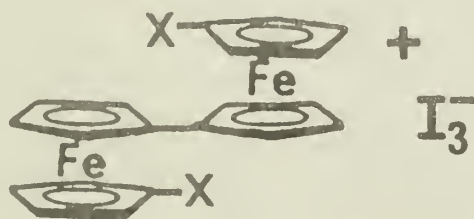
# The Effect of the Solid-State Environment on Intramolecular Electron-Transfer Rates in Mixed-Valence Complexes

Teng-Yuan Dong


Final Seminar

December 17, 1985

The fundamental nature of electron transfer in mixed-valence biferrocenium salts is studied [1]. Various substituents and counterions are employed in order to understand the factors which control electron transfer in the solid state between the two iron ions in mixed-valence biferrocenes. The preparation and characterization of several new series of mixed-valence biferrocenes (1-8), as well as interesting observations on all of the complexes, are described. The rate of thermal electron transfer for a mixed-valence complex in the solid state is characterized by variable-temperature  $^{57}\text{Fe}$  Mössbauer, EPR, and IR measurements [2,3].



1: X = -H

5: X =  $-\text{CH}_2-$  2: X =  $-\text{CH}_2\text{CH}_3$ 

6: X = -I

3: X =  $-\text{CH}_2\text{CH}_2\text{CH}_3$ 

7: X = -Br

4: X =  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ 

8: X = -Cl

A detailed and interesting picture of what controls the electron transfer between the two iron ions in the mixed-valence 1',6'-disubstituted biferrocene cation is emerging. The x-ray structures of 4 [4], 6 [5], and 8 [5] have been determined. The two iron ions are on opposite sides of a planar fulvenide ligand. Compound 8 transfers electrons slower than the Mössbauer time scale at 340 K [5]. On the other hand, 6 and 7 transfer electrons faster than the Mössbauer time scale not only at 298 K, but also all the way down to 4.2 K [4]. Finally, mixed-valence complexes 4 and 5 each show one  $\text{Fe}^{\text{II}}$  and one  $\text{Fe}^{\text{III}}$  doublet in Mössbauer spectra measured below 200 K. As the temperature of these compounds is increased above 200 K the two doublets change to become eventually a single average doublet in the range of 250-275 K. The magnitude of the electronic interaction of the d-manifolds on the two iron ions in a given cation is probably not very different from one cation to another in the 1',6'-disubstituted mixed-valence biferrocenes. Furthermore, the vibronic coupling is also probably not changing very much throughout the series. From an examination of all the data it has become clear that it is the environment about each cation in these solids that is determining whether or not intramolecular electron transfer occurs.



For 6 the x-ray structure shows that the  $I_3^-$  anions are symmetrically disposed relative to the two halves of the cation. In this case it is possible to transfer an electron back and forth between the two iron ions ( $Fe \cdots Fe = 5.1 \text{ \AA}$ ) at a rate in the range of  $10^{10}$ – $10^{12} \text{ sec}^{-1}$  (i.e., faster than EPR, but slower than IR time scale). The x-ray structure of 8 shows the  $I_3^-$  anions are positioned closer to one iron ion of a neighboring cation than the other. This asymmetric environment about a cation dramatically affects the rate at which charge can be pulled back and forth in the cation of 8. The transfer rate for 8 is less than  $10^7 \text{ sec}^{-1}$  at 340 K (via the Mössbauer spectrum).

It is our suggestion that the temperature dependence observed in the Mössbauer spectra for a good crystalline sample of diethyl-, dipropyl-, dibutyl-, and dibenzylbiferrocenium triiodide salts results from a phase transition involving motion of the  $I_3^-$  anion and perhaps the substituents on the cation. At low temperature the  $I_3^-$  ion and biferrocenium cation are fixed in position. As the sample temperature is increased the phase transition temperature is reached and each  $I_3^-$  ion begins to move between two or more positions in the lattice. This transformation could well lead to a dramatic increase in the rate of intramolecular electron transfer. There are actually two possibilities for the movement of the  $I_3^-$  anions. As stated above, it is possible that the  $I_3^-$  anions move as a unit in the solid. However, it is more probable that the  $I_3^-$  anions are interconverting between two configurations, one which can be described in a limiting form as  $I_A^- \cdots I_B - I_C$  and the other one as  $I_A - I_B \cdots I_C^-$ . That is, in each configuration one I-I bond is shorter than the other one in each  $I_3^-$  anion.

The anion dependence of electron transfer rate for the biferrocenium [6] and dihalobiferrocenium [7] cations and endothermic peaks seen in heat capacity [8] and DSC data for biferrocenium triiodide further support the presence of phase transitions. A qualitative model is developed [6] to explain the effect of the anion replacement. The importance of the cation-anion interactions, as well as the intrinsic charge-oscillation barrier heights in the mixed-valence cations and anions, is discussed relative to the phase transition that are believed to be present in these compounds.

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Electron Transfer in Oxo-Centered, Trinuclear,  
Mixed-Valence Iron Acetate Complexes

Seung Mo Oh

Final Seminar

December 19, 1985

The general goal in the study of mixed-valence transition metal complexes has been to understand what factors determine the rate of electron transfer between well-separated metal sites through variation of the bridge between the metal centers [1]. It is frequently implicitly assumed for a symmetric mixed-valence complex that the electronic interaction and the vibronic coupling are the most important factor [2]. In most studies the environment about a mixed-valence complex in the solid state has not been implicated as an important factor controlling the rate of electron transfer.

The electron transfer properties in a series of complexes  $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_3)_6^-(\text{L})_3](\text{S})$  were studied in the solid state where L is an axial ligand such as pyridine or substituted pyridines and S is a solvate molecule such as the corresponding pyridines,  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$  or  $\text{CH}_3\text{CN}$ . It was found in this study that the three-dimensional packing arrangement of the crystalline complexes is the more critical factor for determining the rate of intramolecular electron transfer [3]. This lattice-dependent electron transfer property is believed to be from the fact that the ground state potential energy profile of the mixed-valence system is determined by the solid state packing arrangement. A complex having a more symmetric lattice shows a faster electron transfer rate, which might be due to a smaller difference between the zero-point energy levels of the corresponding nuclear configurations.

Variable-temperature single-crystal X-ray structural results on some of the complexes indicate that there are structural changes in the  $\text{Fe}_3\text{O}$  triangular framework as the sample temperature is varied [3]. It is suggested that the valence-equivalency seen in the Mössbauer spectra of those complexes at higher temperatures is the result of the structural change, rather than a simple thermal activation over the potential energy barrier.

Structural phase transitions have been detected by heat capacity measurements on some of the complexes [4]. In the mixed-valence complex  $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{py})_3](\text{py})$  (1), four phase transitions have been identified. Interestingly, the Mössbauer spectra and the  $^2\text{H}$ -NMR spectra of the sample, in which only the methyl group on the acetate bridge is deuterated, are changed drastically at the phase transition temperatures. In the Mössbauer spectra a third doublet, which is characteristic of the average oxidation state, appears at the low-temperature phase transition (~112 K). The valences of the three iron ions become equivalent in the Mössbauer spectrum at the high-temperature transition (185-190 K). The variable-temperature single-crystal X-ray diffraction study of this same compound indicates that the  $\text{Fe}_3\text{O}$  molecule has a  $\text{C}_3$  axis perpendicular to the  $\text{Fe}_3\text{O}$  triangular unit above the HT-transition point (i.e., three iron atoms are structurally equivalent), but the  $\text{C}_3$  axis disappears at the HT-transition point as the crystal is cooled down. It is clear from these results that there is a direct relationship between the phase transitions and the electron transfer properties of complex 1.



The nature of the phase transitions in complex **1** has been assigned to the three contributions: (1) An electronic transition from a localized to a delocalized state; (2) An order-disorder transition of the pyridine solvate molecule; and (3) An order-disorder transition in the direction of the electronically localized molecular distortion. A  $^2\text{H}$ -NMR study on the pyridine- $\text{d}_5$  analogue of complex **1** indicates an order-disorder transition of the pyridine solvate molecules at the HT-transition point. A theoretical model [5] concerning the possible phase transitions in these mixed-valence complexes has been proposed and the LT-phase transition was explained with this model. It is suggested that the driving force for the ordering of the distorted  $\text{Fe}_3\text{O}$  molecules below the LT-phase transition to be from  $\pi$ - $\pi$  overlapping between the pyridine ligands which belong to the nearest neighboring  $\text{Fe}_3\text{O}$  molecules.

In the closely related complex  $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_3)_6(4\text{-Me-py})_3](\text{C}_6\text{H}_6)$  (**2**), which has the identical structure and similar Mössbauer spectra to complex **1**, the dynamic disorder of the benzene solvate molecules was clearly identified by the single-crystal  $^2\text{H}$ -NMR study [6]. It was found that the benzene molecules rotate about a local  $\text{C}_6$  axis as well as about the  $\text{C}_3$  axis (crystallographic  $c$  axis). This was done by measuring the residual quadrupolar coupling constant and the quadrupolar and dipolar tensors of the benzene deuterons. The faster electron transfer in complex **2** than in complex **1** can be explained by the fact that the  $\pi$ - $\pi$  overlapping between the 4-Me-py ligands is smaller than that for the pyridine ligands in complex **1** and relatively easier rotation of the benzene solvate molecules than the pyridine solvate molecules in complex **1**.

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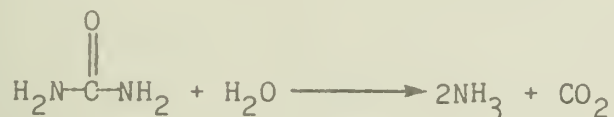
## A Survey of Nickel-Containing Metalloenzymes

Ann E. Ogilvy

Literature Seminar

February 6, 1986

Only in recent years has there been evidence for a possible biological role for nickel. In contrast, almost every first row transition metal can be found in nature. Jack bean urease was the first nickel metalloenzyme to be recognized as such [1,2]. Nickel in jack bean urease is not redox active, but remains in the divalent state throughout its catalytic cycle. Ureases catalyze the hydrolysis of urea to ammonia and carbon dioxide.



The ammonia produced is used by plants, rumen bacteria, and nitrogen-fixing bacteria as a source of nitrogen [3]. The exact geometry of the jack bean urease Ni(II) site is unknown, although electronic absorption spectroscopy combined with inhibition studies using  $\beta$ -mercaptoethanol suggest that the nickel atom is in a pseudo-octahedral environment with three nitrogens and three oxygens attached to the metal [4]. While the mechanism for urea hydrolysis has not been fully elucidated, substrate activation by coordination of the carbonyl oxygen is likely [5]. Since the enzyme has two nickel atoms per subunit, bimetallic mechanisms have also been proposed [3].

Carbon monoxide dehydrogenase (CODH) catalyzes the oxidation of CO to  $\text{CO}_2$ .



Nickel-containing CODH provides energy and a carbon source for acetogenic (acetate producing) and methanogenic (methane producing) bacteria [6]. Electron paramagnetic resonance (EPR) experiments with the enzyme from Clostridium thermoaceticum assign a rhombic signal to a Ni(III) species. Incubation of CODH with CO results in an axial signal and exchange of CO for  $(^{13}\text{C})\text{CO}$  and/or  $^{61}\text{Ni}$ -enrichment ( $^{61}\text{Ni}$ ,  $I = 3/2$ ) confirms the existence of a Ni-C species [7]. Recently, CODH has been proven necessary for acetate metabolism. It appears that the enzyme catalyzes the conversion of coenzyme A to its acyl derivative [9].

Hydrogenase provides energy in the form of electrons for substrate reduction in sulfate-reducing and methanogenic bacteria.

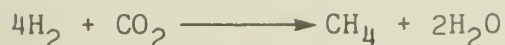


Inactive hydrogenase from Desulfovibrio gigas exhibits a rhombic EPR signal assigned to Ni(III). X-ray absorption fine structure (EXAFS) and x-ray absorption near edge spectroscopy (XANES) conclude that a Ni(III)  $\rightarrow$  Ni(II) reduction occurs upon incubation of the enzyme with hydrogen and that both Ni(III) and Ni(II) coordinate to approximately four sulfur atoms [9]. An intermediate in the hydrogen reduction of hydrogenase has been tentatively assigned to a nickel-hydride species. Two hypothetical redox schemes, one involving Ni(III)  $\rightarrow$  Ni(II) and the other Ni(III)  $\rightarrow$  Ni(0) are currently being investigated using EPR and electrochemical methods [10,11].





Methyldreductase catalyzes the anaerobic reduction of  $C_1$  compounds to methane [12]. Almost all methanogens can utilize  $CO_2$  as their substrate.



Methanogenesis is quite complex, although well characterized compared to the other systems mentioned so far. One mole of enzyme contains two mole of nickel in the form of two mole of F430, a nickel-containing tetrapyrrole so named because of its characteristic absorbance at 430 nm [12]. F430 from Methanobacterium thermoautotrophicum exists both in free form and protein bound. Freshly isolated protein-bound enzyme exhibits a short-lived EPR signal and the nickel atom appears to reside in a tetragonally-distorted octahedral environment with four equivalent nitrogen atoms in the equatorial plane [13]. Sodium dithionite reduces free F430 to give EPR signals matching those of the freshly isolated protein-bound form, suggesting a Ni(I) state. EXAFS experiments on protein-bound F430 provide evidence for octahedral coordination about nickel. Free F430 appears to consist of square planar Ni(II) [14]. In general, Ni(II) complexes with hydroporphinoid ligands exhibit a characteristic conformational ruffling of the ligand system due to the small size and electrophilicity of the nickel ion [15,16]. Axial ligation removes any remaining electrophilicity and thus flattens the tetrapyrrole ring [17].

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Transition Metal Nitrides:  
Some Properties of a Multiply Bonded Ligand

David B. Morse

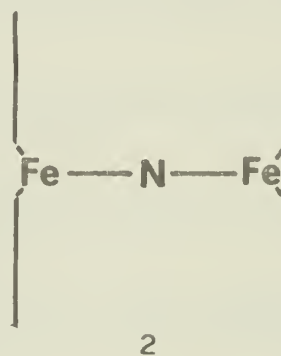
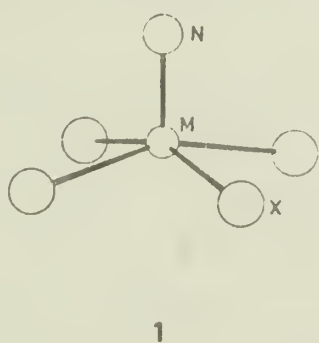
Literature Seminar

February 13, 1986

Stabilization of high oxidation states in inorganic chemistry may be achieved by use of highly anionic ligands, such as nitride ( $\text{N}^{3-}$ ). Nitrides are found in many metal coordination environments, ranging from terminally bound nitrides [1] to multi-metal imides [2] and interstitial nitrogen clusters [3]. Those compounds in which nitrogen is bound to three metals or less are in a group of nitrides whose syntheses are relatively well established, but which have only recently been examined for their physical properties.

The successful synthesis of metal nitrides has centered primarily on the use of an azide derivative (such as sodium azide, a halo-azide ( $\text{ClN}_3$ ), or trimethylsilylazide ( $\text{Me}_3\text{SiN}_3$ )) and a metal halide. Generally, nitride compounds are oxygen and water stable, and are isolated in high yields (60-80%). By far the most extensive characterization of nitrides has been by infrared spectroscopy ( $\nu(\text{MN})=1150-950\text{ cm}^{-1}$ ) and x-ray crystallography ( $r(\text{MN})=1.5-1.7\text{ \AA}$ ). The reactivity of nitrides is limited by the weak nucleophilicity of the nitrogen and its strong trans-labilizing effect, although ligand exchange reactions are common and provide routes to new nitride complexes [4].

Nitrides are among the strongest known  $\pi$ -donating ligands, second perhaps only to carbynes, and as such investigations into their bonding characteristics can yield useful information on ligand bonding effects, as well as interesting comparisons with other  $\pi$ -donating ligands (e.g., metal-oxo species,  $\text{M}=\text{O}$ ) [5]. One of the more well studied compound classes, the isostructural  $d^0$ ,  $d^1$ , and  $d^2$  tetrahalo metal nitrides ( $\text{MNX}_4$ , 1) [6]. Electron spin resonance (Esr) studies

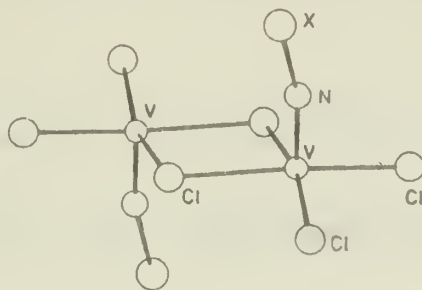


have indicated that valence electrons occupy mainly metal- $d_{xy}$  based molecular orbitals, and have provided atomic orbital coefficients in molecular orbital calculations [7]. Esr has also shown the greater  $\pi$ -bonding characteristics of nitrides over analogous oxo compounds. Similarly, preliminary investigation of bis(porphinatoiron)nitride ( $[(\text{TPP})\text{Fe}]_2\text{N}$ , 2) as a member of the series  $(\text{PFe})_2\text{X}$  ( $\text{X}=\text{C}, \text{N}, \text{O}$ ) has illustrated the effects of varying degrees of  $\pi$ -bonding on the molecular orbitals of bridged dimers [8].





One of the more unique classes of metal-nitrogen compounds are the halonitrenes, best illustrated by  $\text{Cl}_3\text{VNCl}$  and its derivatives. With a formal N-Cl single bond, these compounds exhibit metal nitrogen distances typical of triple



bonds, and have magnetic moments indicating a high degree of vanadium-nitrogen multiple bonding [9]. These complexes display no nitrogen nucleophilicity, and the reactions of these compounds occur almost without exception at vanadium. The halogen is not labile. Some recent work has indicated that  $\text{Cl}_3\text{VNCl}$  may prove to be a good nitride transfer reagent to later-series transition metal complexes [10].

The future of inorganic nitride chemistry may well expand along several fronts. Physical measurements on the bonding in nitrides are not yet complete, nor are studies into the trends between carbide, nitride, and oxide as strong  $\pi$ -donating ligands. Apparently untouched in physical analyses are the mixed valence bimetallic nitrides, for which several examples may exist. Areas also needing attention include a) expansion of the known nitrides past Group 6, 7, and 8, b) organometallic nitride examples, and c) increasing the available metal and  $^{15}\text{N}$  NMR data on nitrides.

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# Discontinuous Thermochromic Phase Transitions in Transition Metal Salts

Michael D. Lowery

Literature Seminar

March 4, 1986

A thermochromic material is a substance which changes color as a function of temperature. A particularly interesting class of thermochromic materials involves transition metal salts that exhibit an abrupt color change which is the result of a structural phase transition [1]. These types of discontinuous thermochromism are associated with changes in coordination geometry and/or ligand field strength.

For copper halide salts, discontinuous thermochromism has been known for some time. For certain quaternary salts of  $\text{CuCl}_4^{2-}$ , the green to yellow thermochromic transition results from a change in the anion geometry from square planar to a less crowded distorted tetrahedral configuration [2]. Willett et al. have proposed that the phase transition in these salts results from the weakening of hydrogen bonding and crystal packing forces in the high temperature phase [3].

Discontinuous thermochromism of copper(II) and nickel(II) complexes of N,N-diethylethylenediamine have also been known for some time. The  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ , and  $\text{NO}_3^-$  salts of the copper(II) derivative all exhibit an abrupt change from brick red to deep violet at the phase transition. A number of workers postulated that the thermochromic transition resulted from increasing axial interaction of the anion which resulted in the formation of a tetragonally distorted octahedral arrangement [4]. Recently, however, it has been shown via X-ray analysis and NMR studies that the color change results from a decrease in the ethylenediamine ligand field strength due to rapid flipping of the ethylenediamine chelate ring [5].

Mori and coworkers have investigated the sudden purple-to-green transition of  $\text{Cu}(\text{NO}_2)_2(\text{NH}_3)_2$  [6]. By comparing the infrared spectra of the two phases it was concluded that the color change results from linkage isomerization of the  $\text{NO}_2^-$  ligand. Below the transition temperature  $\text{NO}_2^-$  is coordinated through the nitrogen atom while in the green phase it is oxygen bound. Mori has also found it possible to "fine-tune" the transition temperature from approximately -50 to 30 C by partially replacing the  $\text{NO}_2^-$  ligand with chloride or bromide ions.

One of the oldest examples of discontinuous thermochromism is found in the transition metal salts of the  $\text{HgI}_4^{2-}$  anion. The mechanism of the phase transition has been shown to be an order-disorder transition with the cations being ordered below the transition temperature and disordered above the phase transition temperature [7]. These compounds have received renewed interest as they show high electrical conductivity above the phase transition (due to the increased mobility of the cations). Because they also contain a very reproducible hysteresis loop they may be suitable for use as a high density, erasable IR recording medium.

The phenomenon of thermochromism in inorganic compounds gives one an opportunity to gain much insight into the processes which occur during a solid state phase transition. In only a relatively few complexes have investigations of the static and dynamic nature of the thermochromic transition been undertaken.





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## Highly Reduced Organometallic Complexes of the Vanadium and Chromium Triads

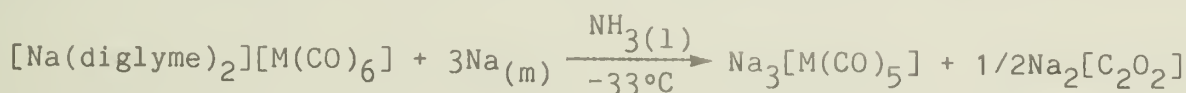
Dave Dempsey

Literature Seminar

March 6, 1986

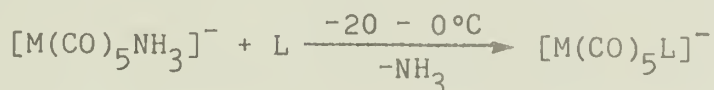
Transition metal carbonyl anions and dianions can be regarded as mimics to the halides and chalcogenides with regard to their reaction chemistry [1]. In 1977 John Ellis reported the synthesis of the first metal carbonyl trianions,  $[\text{Mn}(\text{CO})_4]^{3-}$  and  $[\text{Co}(\text{CO})_3]^{3-}$  [2]. Existence of these highly reduced trianions suggested that an entire family of super reduced metal carbonyls might exist.

Ellis and coworkers were able to reduce group 5 metals with  $\text{Na}_{(m)}$  in liquid  $\text{NH}_3$  [3].

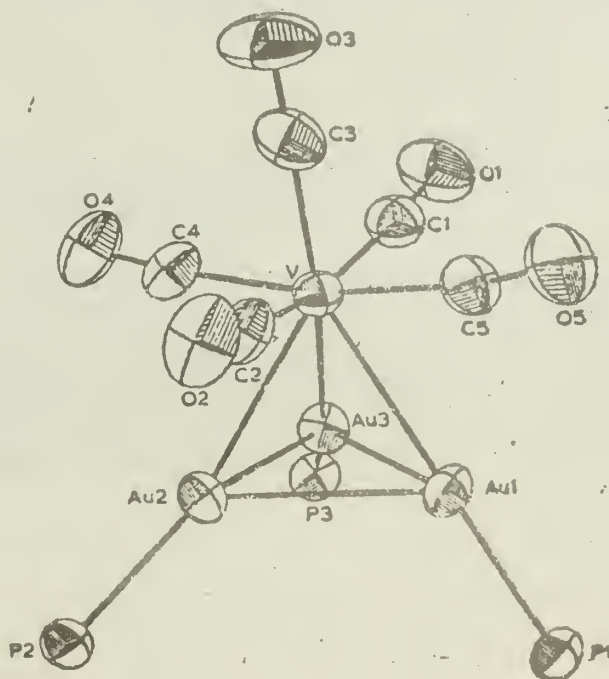


$\text{M} = \text{V}, \text{Nb}, \text{Ta}$

Metathesis of  $\text{Na}_3[\text{V}(\text{CO})_5]$  with  $\text{MCl}$  ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ ) yields slightly more stable complexes. The IR spectrum of  $\text{Cs}_3[\text{V}(\text{CO})_5]$  shows carbonyl stretches at 1800, 1626, 1563  $\text{cm}^{-1}$ , indicating the occurrence of extensive  $\pi$ -backbonding. Attempts to form the hydride anion,  $[\text{HM}(\text{CO})_5]^{2-}$ , by reacting the trianion with  $\text{NH}_4\text{Cl}$  resulted in the generation of  $[\text{M}(\text{CO})_5\text{NH}_3]^-$ . This highly unstable complex undergoes facile exchange reactions in the presence of  $\pi$ -acceptor ligands [4].



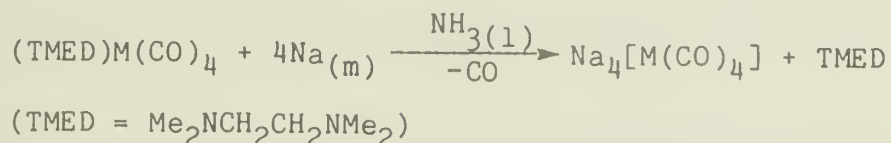
Previous attempts to synthesize the products have resulted in both mono- and disubstituted products [5].  $\text{Na}_3[\text{V}(\text{CO})_5]$  formed  $(\text{Ph}_3\text{PAu})_3\text{V}(\text{CO})_5$  when treated with 3 equivalents of  $\text{Ph}_3\text{PAuCl}$ . An X-ray structure analysis revealed the complex to be a tetrahedral Au-V cluster, the first 8-coordinate vanadium complex (see figure below) [6].



Crystal Structure of  $(\text{Ph}_3\text{PAu})_3\text{V}(\text{CO})_5$



Unlike the Group 5 metals, direct reduction of  $\text{Na}_2[\text{M}(\text{CO})_5]$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) gave no isolable products [7]. However reduction was accomplished by Ellis' "labilization reduction" method [7] in which a labile ligand is displaced during the reaction:



Reaction of the tetraanions with excess  $\text{NH}_4\text{Cl}$  generated the diammine complex  $\text{M}(\text{CO})_4(\text{NH}_3)_2$ . Curiously, when the tetraanions were treated with 2-3 equivalents of  $\text{NH}_4\text{Cl}$  formation of the dihydride dianion,  $[\text{H}_2\text{M}_2(\text{CO})_8]^{2-}$ , is observed [7]. The tungsten dihydride when reacted with 2 equivalents of  $\text{K}[\text{sec-Bu}_3\text{BH}]$  generated the dihydride dianion monomer:



In contrast, reaction with the molybdenum analog gave  $[\text{HMo}(\text{CO})_3]_4^{4-}$  cluster [8].

Reduction of  $(\text{PMTA})\text{W}(\text{CO})_3$  (PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine) with 6 equivalents of  $\text{K}_{(\text{m})}$  gave an uncharacterized product "X" in low yields [9].



When "X" reacted with 6 equivalents of  $\text{Ph}_3\text{SnCl}$  followed by metathesis with  $\text{Et}_4\text{NCl}$  in ethanol (EtOH) gave  $[(\text{Ph}_3\text{Sn})_2\{(\text{Ph}_2\text{Sn})_2\text{OEt}\}\text{W}(\text{CO})_3]^-$  [9]. An x-ray structure analysis of the isopropanol analog shows a bidentate  $[(\text{Ph}_2\text{Sn})_2\text{O-i-Pr}]$  ligand formed from the cleavage of Sn-C bond [10]. Solution IR studies indicate the Sn-C bond is cleaved before the metathesis [9].

Highly reduced transition metal carbonyl anions possess interesting bonding characteristics and can be used as precursors for the synthesis of new organo-metallic compounds. The synthesis of other highly reduced complexes, such as the presently unknown  $[\text{Ti}(\text{CO})_6]^{2-}$ , and further study of the reactivity of such complexes is underway in several laboratories.

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Chemistry of Octaethylporphyrinatorrhodium Hydride  
and Octaethylporphyrinatorrhodium(II) Dimer

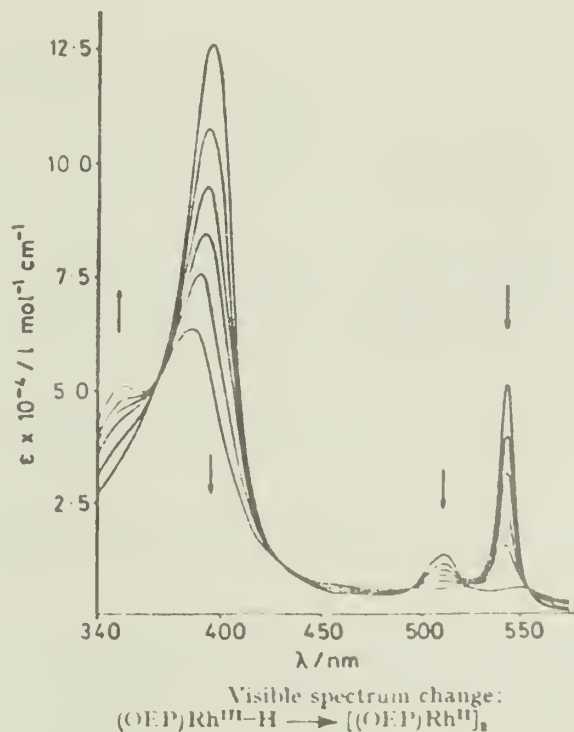
Thomas G. Gardner

Literature Seminar

April 1, 1986

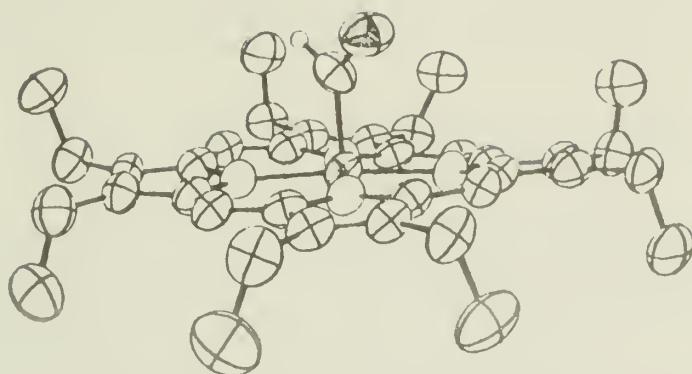
Interest in rhodium porphyrins originated in the biomimetic chemistry of cobalt complexes, such as vitamin B-12 [1,2,3]. However, many unique aspects of rhodium porphyrin chemistry have been observed. Rhodium(III)-carbon bonds have higher bond dissociation energies (i.e., are thermally more stable) than their cobalt(III) analogues [3]. Some rhodium porphyrin complexes provide models for intermediates in the water gas shift reaction (WGSR) [4] and in the Fischer-Tropsch reaction [5]. In addition, rhodium(II) porphyrins tend to exist as diamagnetic dimers with the rhodium centers singly bonded [6,7,8]. This metal-metal bond is easily homolyzed [9,10] to produce a highly reactive "metallo-radical" intermediate, which reacts with aromatic hydrocarbons [9,10], carbon monoxide, and olefins [11].

Octaethylporphyrinatorrhodium(III) hydride ( $\text{OepRhH}$ ) is in equilibrium with octaethylporphyrinatorrhodium(II) dimer ( $(\text{OepRh})_2$ ) and molecular hydrogen in benzene solution [6,7,8]. Therefore, any reaction involving  $\text{OepRhH}$  will also occur with  $(\text{OepRh})_2$  in the presence of dihydrogen. The conversion of  $\text{OepRhH}$  to  $(\text{OepRh})_2$  may be followed with visible spectroscopy, as shown below [13]:



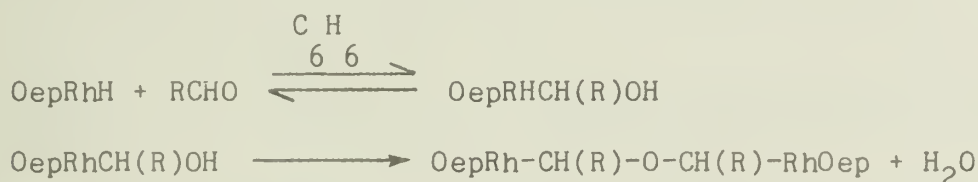
$\text{OepRhH}$  reacts reversibly with carbon monoxide to give a formyl complex,  $\text{OepRh}(\text{CHO})$  [4,11,13]. This formyl complex is represented by the ORTEP diagram given below:



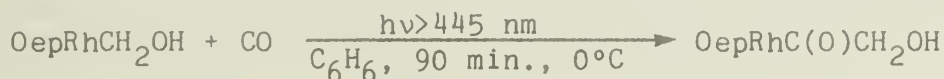


ORTEP representation for RhOEP(CHO). Bond lengths and angles for the RhCHO unit are as follows: Rh-C, 1.896 (6) Å; C-O, 1.175 (5) Å; C-H, 1.09 (1) Å; Rh-C-O, 129.6 (5)°; Rh-C-H, 129.9 (4)°.

This represents the first example of a formyl formed directly from a metal hydride and carbon monoxide (or from a metal complex,  $(\text{OepRh})_2$ , with dihydrogen and carbon monoxide). The infrared spectroscopic study of this species indicates that metal-carbonyl back-bonding is not significant in the formyl; therefore, this functional group is likely to exhibit reactivity similar to organic aldehydes.  $\text{OepRhH}$  nucleophilically adds to aldehydes, yielding hydroxyalkyl rhodium octaethylporphyrin [5,15], which can eliminate water to form a symmetrical metallo-ether [5]:



The hydroxymethyl complex also reacts with excess  $\text{OepRhH}$  to reductively eliminate methanol, the first such example from a hydroxymethyl intermediate. Carbon monoxide can be inserted into the rhodium-carbon bond of the hydroxymethyl complex, providing a pathway to a two-carbon organic molecule.

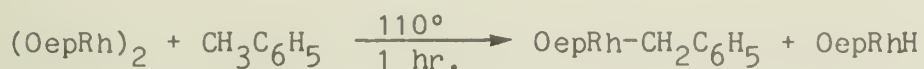


The addition is believed to occur through free radical intermediates, and the stereochemistry is guided primarily by steric effects.

The key feature of the chemistry of  $(\text{OepRh})_2$  is its ability to undergo homolysis of the rhodium-rhodium bond, leaving a paramagnetic intermediate, which can react with Lewis bases by a general mechanism characteristic of free radical reactions. An example of the mechanism is the Arbusov rearrangement of trimethyl phosphite to the phosphonate catalyzed by  $(\text{OepRh})_2$  [16]. In the presence of water, carbon monoxide reacts with  $(\text{OepRh})_2$  to yield the formyl,  $\text{OepRhCHO}$ , the carbon dioxide [4]. Since the formyl can equilibrate back to  $\text{OepRhH}$  and carbon monoxide, and photolysis of  $\text{OepRhH}$  yields  $(\text{OepRh})_2$  and molecular hydrogen, the  $(\text{OepRh})_2$  dimer shows potential for use as a WGS catalyst.



Aromatic hydrocarbons (e.g., toluene, ethylbenzene, etc.) are observed to react with  $(\text{OepRh})_2$ , resulting in the activation of the carbon-hydrogen bond alpha to the aromatic ring, and yielding a benzyl derivative [9,10].



With longer chain alkyl groups, rearrangement occurs slowly to yield products with rhodium-carbon bonds in alkyl positions other than alpha. The  $(\text{OepRh})_2$  dimer also reacts with styrene [11], acetylenes [6,13,17], and ethyl vinyl ether [12,13,17] to give products in which the unsaturated carbon-carbon bond has inserted into the rhodium-rhodium bond of the dimer.



Current investigations into the chemistry of  $\text{OepRhH}$  and  $(\text{OepRh})_2$  involve the heterolytic cleavage of the rhodium-rhodium bond of the dimer by a strong Lewis base donor ligand such as pyridine. There is also ongoing interest in completing a Fischer-Tropsch catalytic cycle using  $\text{OepRhH}$  as the active catalyst.

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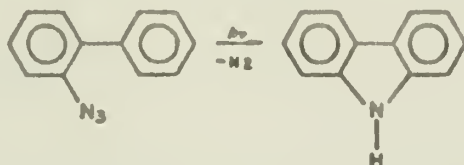
## Ligand Photofragmentation of Metal Complexes

Stephen J. Doktycz

Literature Seminar

April 1, 1986

Photofragmentation or photoelimination reactions have been a valuable means of generating reactive intermediates in organic chemistry for many years. These photoreactions are initiated by the cleavage of a sigma bond and result in net rearrangement, fragmentation, or elimination of a small molecule (e.g.  $N_2$ , CO,  $CO_2$ , etc.)

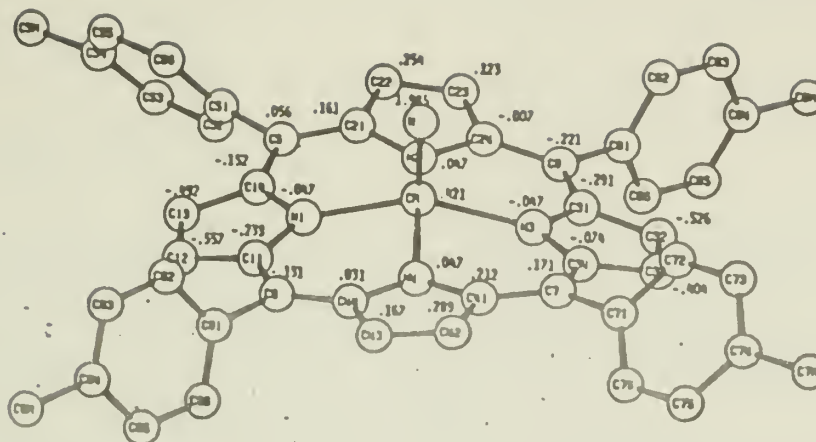


The application of this general type of photoreaction to transition metal coordination compounds has been found to give interesting results.

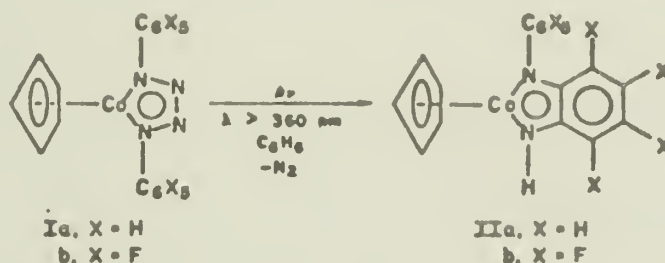
Ultraviolet irradiation of transition metal oxalate complexes leads to irreversible fragmentation of the oxalate ligand into two molecules of carbon dioxide concomitant with two electron reduction of the metal [1]. In 1969 Nyman [2] suggested that photolysis of  $M(PPh_3)_2(C_2O_4)$  ( $M=Pt(II), Pd(II)$ ) might produce the 14 electron  $M(PPh_3)_2$  ( $M=Pt(0), Pd(0)$ ) fragment as the reactive intermediate in the absence of competing ligands. Indeed, he found that  $Pt(0), Pd(0)$  complexes could be isolated from the photochemical reactions [3]. Later, Trogler et al. working with  $Pt(PET_3)_2(C_2O_4)$  found that  $Pt(PET_3)_2$  could be generated in situ upon UV irradiation [4]. The existence of the  $Pt(PET_3)_2$  fragment was supported by the following experimental facts: (1) irradiation of solutions of  $Pt(PET_3)_2(C_2O_4)$  in the presence of donor and acceptor ligands L, lead to formation of  $Pt(PET_3)_2L_n$  (2) the compounds  $Pt(PET_3)_2XY$  can be formed if the platinum(II) oxalate species is irradiated in the presence of oxidative addition substrates XY (3) two equivalents of carbon dioxide per equivalent of starting material are evolved and (4) each product contains the  $Pt(PET_3)_2$  moiety.

The coordinated azide ligand has been the subject of many photochemical investigations. The azide ligand has been observed to decompose via three routes. The azidopentacyano complexes of  $Rh(III)$  and  $Ir(III)$  have been found to eliminate the  $N_3^-$  anion upon photoaquation. Alternatively, the azido complexes of  $Pt(II)$ ,  $Au(III)$ , and  $Co(NH_3)_5N_3^{2+}$  produced azide radicals from photoredox chemistry. And thirdly, the azidopentaamines of  $Rh(III)$  and  $Ir(III)$  were found to form coordinated nitrenes [5]. The differences in photoreactivity of these azido ligands were attributed to: ligand back-bonding interactions in the CTM excited state, metal to ligand charge transfer [6], and efficiencies of internal conversion processes. Later work with other transition metals showed that photolysis of  $Cr(NH_3)_5N_3^{2+}$  also proceeded via the nitrene pathway [7] and that redox and nitrene modes of reaction occurred in competition. Recently, nitrido-(porphyrinato) $M(V)$  ( $M=Cr, Mn$ ) complexes have been synthesized using this technique [8].





Paralleling azido photochemistry, the diaryltetraazadiene ligand in cyclopentadienylcobalt 1,4-diaryltetraazadiene was found to also extrude  $N_2$  upon photolysis [9]. The final product was believed to form through the insertion of



one coordinated nitrene into the ortho C-H bond of its partner followed by a subsequent [1,3] (N,Co,N) suprafacial hydrogen shift.

Both the azido and diaryltetraazadiene ligands were found to extrude di-nitrogen upon photolysis and result in coordinated nitrene products and their derivatives whereas the photolysis of the oxalato-bis(phosphine) Pt complexes resulted in a reactive coordinatively unsaturated bisphosphine Pt(0) intermediate. All three are examples of the use of photochemistry to produce new molecules through reactive metal-centered intermediates. Further directions of research could include the adaption of these ligands to other metal centers or possibly the use of this idea on as yet untried ligands such as coordinated azo compounds.

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## A Thermodynamic and Electronic Explanation of the Macrocyclic Effect

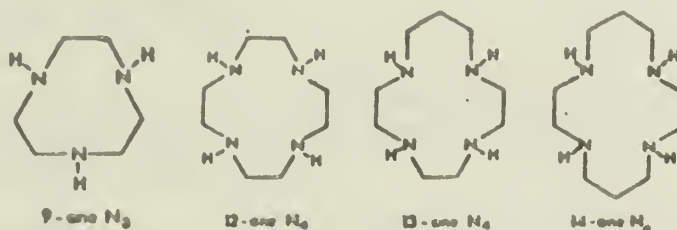
Warren A. Kaplan

Literature Seminar

April 8, 1986

The extra stability of the complexes of macrocyclic ligands over that of their open-chain analogs has been termed the macrocyclic effect [1]. In addition to the extreme thermodynamic stability, macrocyclic complexes display a stronger ligand field than do their open-chain analogs, provided that the "hole" is not too large for the metal ion [2].

Based upon the ligand field splitting parameters for various tetraaza macrocyclic complexes of cobalt and nickel, D. H. Busch originally suggested that the high ligand fields were due to compression of the metal ion [3]. Recent empirical force-field calculations on complexes of the macrocyclic ligands shown below were carried out and the results show the compression hypothesis to be incorrect. Rather, it appears as though the largest ligand field is obtained for the macrocycle which bonds to the metal ion with the least strain in the metal-nitrogen bond [4].



Gas phase enthalpy data [5] clearly show the greater inductive effects of secondary nitrogens relative to primary ones. It is believed that the increased ligand field strength of the macrocycle over the open-chain analog is due to this increased inductive effect of the extra secondary nitrogens found in the macrocyclic ligand [6].

The thermodynamic stability of tetraaza macrocyclic complexes seems to have contributions both enthalpic and entropic in origin. It is generally agreed that the entropy contribution arises from the smaller configurational entropy of the macrocycle, and it is the enthalpy contribution that requires explanation [4].

The inductive effect of the secondary nitrogens is a contributor to the macrocyclic enthalpy. Empirical force-field calculations carried out by R. D. Hancock also shows that steric "pre-straining" of the macrocyclic ligand contributes to the macrocyclic enthalpy [6]. Thermodynamic studies on mixed-donor macrocycles of oxygen and nitrogen [7], and sulfur and nitrogen [8] show that this pre-straining may be modified by steric hindrance to solvation in aqueous solution. This evidence is not conclusive however.

An interesting property of tetraaza macrocycles appears to be an anomalous metal ion size selectivity [9]. Very large metal ions complex most strongly to a relatively small macrocycle (12-aneN<sub>4</sub>), while smaller metal ions prefer an intermediate sized macrocycle (14-aneN<sub>4</sub>) [10]. The reason for this phenomenon



is shown by molecular mechanics calculations to be due to the ability of the tetraaza macrocycles to adopt various conformations upon complexation to the metal ion [11].

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# The Chemistry of Some Triosmium Alkylidene and Alkylidyne Cluster Complexes

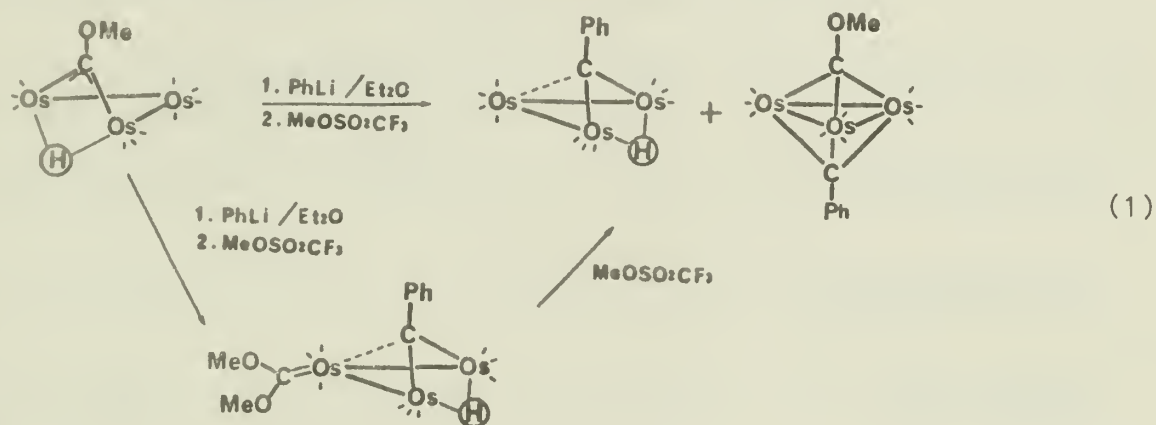
Wen-Yann Yeh

Final Seminar

April 24, 1986

The chemistry of metal cluster complexes containing alkylidene ( $=\text{CR}_2$ ) or alkylidyne ( $\equiv\text{CR}$ ) ligands has been of interest for many years [1]. This interest has intensified due to the implication of surface-bound  $\text{C}_1$  and  $\text{C}_2$  units in some catalytic reaction mechanisms, such as alkyne (alkene) metathesis [2], alkyne (alkene) oligomerization [3], and Fischer-Tropsch synthesis [4].

Previous studies by Shapley and co-workers [5] established that sequential  $\text{H}^-/\text{H}^+$  treatment of  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-COMe})$  affords  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CH})$  via an alkylidene intermediate  $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-CHOMe})^-]$ . However, an analogous  $\text{Ph}^-/\text{Me}^+$  treatment of  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-COMe})$ , occurring at a carbonyl ligand, leads to formation of a mixed alkylidene-alkylidyne complex  $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\eta^1\text{-C(OMe)}_2)(\mu_3\text{-CPh})$  [6]; furthermore, extended treatment of  $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\eta^1\text{-C(OMe)}_2)(\mu_3\text{-CPh})$  with  $\text{MeOSO}_2\text{CF}_3$  gives the alkylidyne complexes,  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CPh})$  [7] and  $\text{Os}_3(\text{CO})_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$  [8] (eq. 1). These compounds have been characterized by mass, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies together with single-crystal X-ray diffraction analysis (by Churchill and coworkers).



Further studies of sequential  $\text{Ph}^-/\text{Me}^+$  reactions with  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CPh})$ ,  $\text{Os}_3(\text{CO})_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$ , and  $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\eta^1\text{-C(OMe)}_2)(\mu_3\text{-CPh})$  have been conducted. It appears that sequential  $\text{Ph}^-/\text{Me}^+$  treatment is effective for the transformation of carbonyl ligands to alkylidene and alkylidyne moieties. Moreover, by repeating this two-step procedure, dialkylidyne and mixed alkylidene-alkylidyne complexes can be prepared. The overall predictability of this treatment, however, is low.

Several reactions of these compounds have been investigated, such as hydrogenation, pyrolysis, carbonylation, protonation, ligand substitution, and reactivity toward Lewis acids. The stereodynamics of fluxional cluster complexes have been studied by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The reactivity of alkylidyne and alkylidene ligands have been examined; examples include alkylidyne-alkylidyne coupling with  $\text{Os}_3(\text{CO})_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$ , alkylidyne-carbonyl coupling with  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CPh})$ , alkylidyne-alkylidene coupling with  $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\eta^1\text{-C(OMe)}_2)(\mu_3\text{-CPh})$ , alkylidyne-alkyne coupling with  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CPh})$ , and benzylidyne-tolyne interconversion with  $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CPh})$  and  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3, \eta^2\text{-C}_6\text{H}_3(\text{CH}_3))$ .





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Poly(sulfur nitride),  $(\text{SN})_x$ ,  
Synthesis, Structure, and Conductivity

Steven D. Gammon

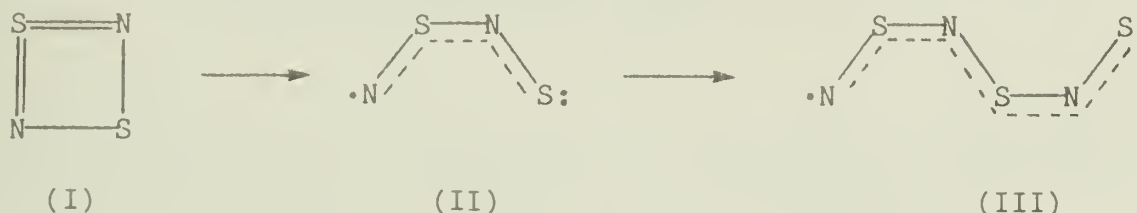
Literature Seminar

May 6, 1986

Poly(sulfur nitride),  $(\text{SN})_x$ , is a compound that has attracted great attention in the scientific community in the last 15 years. Studies have concentrated on a wide variety of areas: synthesis, physical and electronic structure, formation, and electrical properties [1]. Perhaps the most striking aspect of  $(\text{SN})_x$  is its metal-like properties of high conductivity (on the order of mercury), metallic reflectivity, and the superconductive transition at 3K. Despite the large number of publications on  $(\text{SN})_x$ , only recently has a consistent picture of the properties begun to emerge.

Poly(sulfur nitride) was first synthesized by F. P. Burt in 1910 [2]. His method consisted of passing hot  $\text{S}_4\text{N}_4$  vapor through silver or glass wool and collecting the resulting  $\text{S}_2\text{N}_2$  on a cold finger and allowing it to polymerize to  $(\text{SN})_x$ . In many respects, this mode of synthesis has not undergone drastic revision [3]. In addition to the above method, there have been some more recent synthetic routes which include the low temperature polymerization of  $\text{S}_4\text{N}_2$  in THF [4], the high temperature reaction of  $\text{S}_4\text{N}_3\text{Cl}$  and silver wool [5], the decomposition of  $\text{Ph}_3\text{P}=\text{NSN}=\text{S}=\text{S}$  [6], and others [7]. There have also been some chemical (soln) reactions [8] and electrochemical synthesis [9].

To gain an understanding of the electrical properties of  $(\text{SN})_x$  several studies of the solid-state polymerization of  $\text{S}_2\text{N}_2$  have been carried out. Early theories [2] involved a simple ring cleavage of the  $\text{S}_2\text{N}_2$  unit and the subsequent "chain reaction" formation of the polymer.

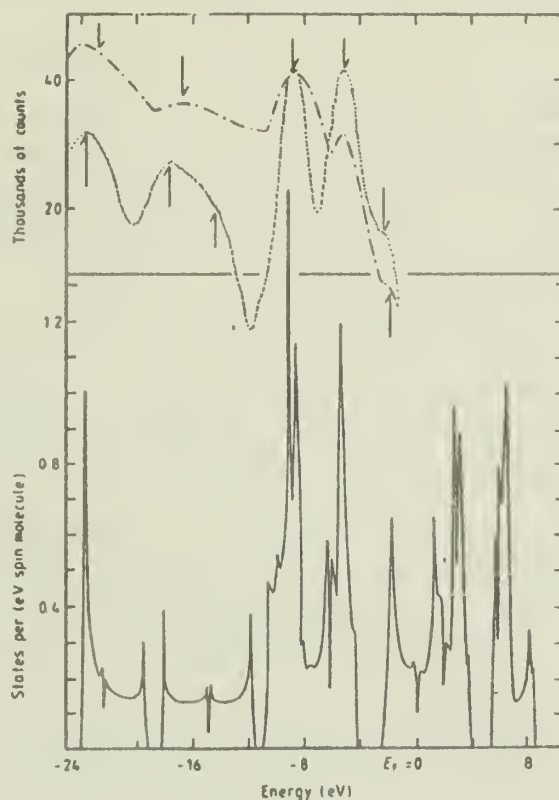


Molecular orbital studies predict that the driving force for the reaction might involve the "development" of a new sigma orbital in the open form (II) that was formerly an antibonding pi orbital in (I) [10]. An alternate theory postulates that the d orbital functions are involved in electron delocalization which leads to an extravalent N---S d function interaction driving the dimerization at 4 Kcal/mole [11]. Structural studies have revealed that during the polymerization process there is substantial crystal imperfection due to crystal twinning, an event which ultimately is responsible for the compound's electronic properties [12].

In addition to electronic formation studies, there have been many views of the electronic structure of the polymer. One study predicts that in the idealized single chain linear structure there is a metal-insulator Pierls distortion manifested in a charge density wave (CDW) [13]. Interchain interaction and defect sites are responsible for suppressing the metal to insulator 1-D transition. Band structure calculations have ranged from the early 1-D structure postulate, to two recent structures that predict that the conductivity is due to



degenerate pi orbitals at the Fermi level rendering the Pierls distortion ineffective at suppressing the metallic conductivity [14]. X-ray photoelectron spectrum (XPS) has shown that the density of states at the Fermi level to be 0.14 states per (eV spin molecule) as predicted in above model (Fig. IV) [14].



Comparison of the density of states obtained by the present calculation (full curve) with the XPS results reported by two different experimental groups, the chain curve obtained by Ley and the dotted curve obtained by Mengel *et al.*

(IV)

Polarized reflectivity spectra in the VUV region found that the tight binding band model is successful in describing the electronic structure [15]. It also postulates that the conduction takes place in a 1-D manner in the conduction band involving electron and hole gaps above the Fermi surface.

One of the properties still undergoing debate is how conductivity varies with temperature. Early measurements of conductivity record an increase of conductivity to approximately 30 K at which point, the conductivity decreases. Recently, it has been shown that the conductivity increases down to the superconducting transition [16]. This new data supports current thinking that  $(\text{SN})_x$  should be considered a 3-D semi-metal.

The future of  $(\text{SN})_x$  and related chemistry promises to be fruitful. There are already several patents of applications in diodes and batteries. The intercalate with bromine,  $(\text{SNBr}_y)_x$ , has shown to have conductivities on the order of  $10^3$  times greater than undoped  $(\text{SN})_x$ . Future studies of related compounds— $(\text{SeN})_x$ —for example, might prove to have electrical properties that surpass  $(\text{SN})_x$  in metallic behavior.  $(\text{SN})_x$  promises to be the first in a class of metallic main group compounds with a host of unique properties.





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The Chemistry of Highly Electronegative  $\text{OTeF}_5$  Group

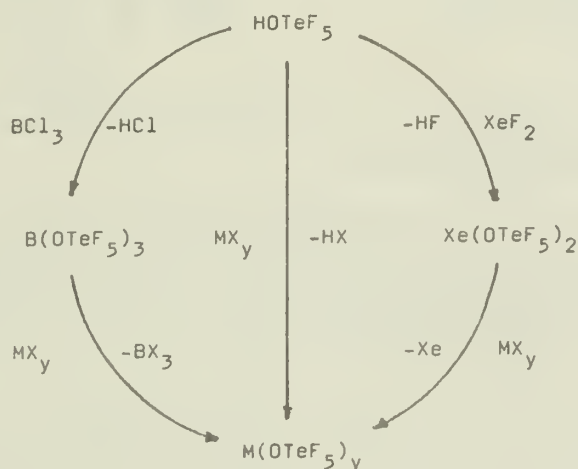
Jayantha Amarasekera

Literature Seminar

May 6, 1986

After the discovery of pentafluoroorthotelluric acid,  $\text{HOTeF}_5$ , it soon became clear that the chemistry of pentafluoroorthotellurate,  $-\text{OTeF}_5$  (also called teflate) group, is almost as extensive as that of fluoride [1]. The ability of this ligand to stabilize the highest valency levels of the central atoms to which it is bound is unsurpassed by any other polyatomic ligand. Because of the ligand's size and internal bonding it hardly ever forms bridges, and in this respect it differs from fluorine, although it does share the latter's high electronegativity.

The methods for the preparation of teflate compounds are many. In accord with the high acidity of teflic acid ( $\text{HOTeF}_5$ ), proton displacement reactions are frequently performed, affording ionic as well as covalent teflate compounds. A versatile source of the  $\text{OTeF}_5$  group is  $\text{B}(\text{OTeF}_5)_3$  [2]. The advantage of this reagent is that treatment with fluorides give volatile  $\text{BF}_3$  as a byproduct. The xenon derivative,  $\text{Xe}(\text{OTeF}_5)_2$ , can be used to introduce the  $\text{OTeF}_5$  group oxidatively [1], (Scheme 1)



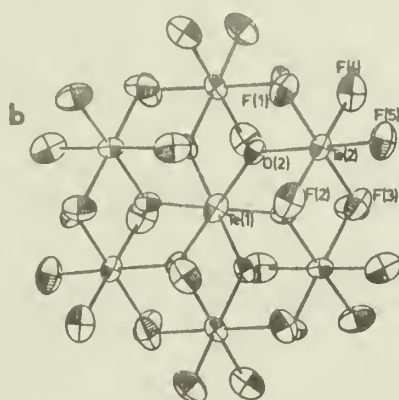
Scheme 1.

The teflate group is capable of stabilizing different oxidation and coordination states, due to its bulkiness and high electronegativity. The anion radius for  $\text{OTeF}_5$  has been computed from crystallographic data for  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  salts. This anion is slightly larger than the iodide ion. Structural studies (group site preference) [3], NMR chemical shifts [4], Mössbauer isomer shifts [5] and chemical reactivity studies [2] indicate the electronegativity of  $\text{OTeF}_5$  and F are practically equal. As estimated from  $^{129}\text{Xe}$  Mössbauer quadrupole splittings the electronegativity of  $\text{OTeF}_5$  is 3.87 (Pauling scale) compared to 3.98 for F [5]. A rationale for this high electronegativity is certainly the inductive effect of the five fluoride, which additionally promotes ( $p\pi - d\pi$ ) back bonding from oxygen to tellurium. Due to this high electronegativity of teflate group, xenon teflates,  $\text{Xe}(\text{OTeF}_5)_2$ ,  $\text{Xe}(\text{OTeF}_5)_4$  and  $\text{Xe}(\text{OTeF}_5)_6$  are the most stable xenon compounds known after their fluorides [6].

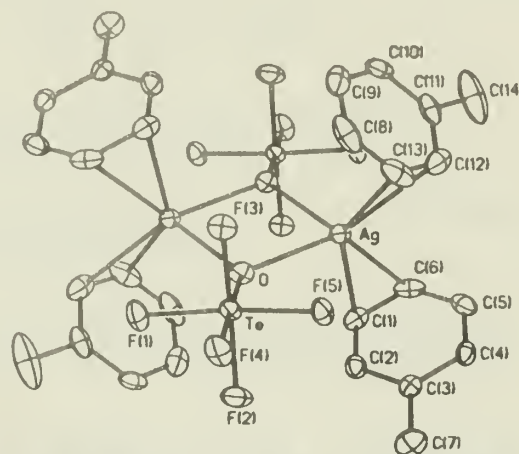




The elements in the first transition period have a tendency to form tetrahedral teflates. For example,  $\text{Ti}(\text{OTeF}_5)_4$  is a rare example of titanium in a tetrahedral  $\text{O}_4$  coordination site [7]. The larger central atoms uranium and tungsten permit relatively simple formation of heavy molecules  $\text{U}(\text{OTeF}_5)_6$  and  $\text{W}(\text{OTeF}_5)_6$  [8]. Some oxo-teflates include  $\text{VO}(\text{OTeF}_5)_3$ ,  $\text{MoO}(\text{OTeF}_5)_4$  and  $\text{O}_2\text{Re}(\text{OTeF}_5)_4$ , the only teflate with a heptavalent central atom [8].  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$  can be considered as the first low valent transition metal teflate [9]. Bridging  $\text{OTeF}_5$  ligands have not been observed or suggested until the very recent discovery of  $\text{Ag}(\text{OTeF}_5)$  [10] and  $\text{Au}(\text{OTeF}_5)_3$  [11].



$\text{Te}(\text{OTeF}_5)_6$  molecule, projected along the 3 axis:



ORTEP drawing of the centrosymmetric molecule  $[\text{AgOTeF}_5(\text{C}_6\text{H}_5\text{CH}_3)_2]_2$  (50% probability ellipsoids, hydrogen atoms omitted).

The properties of many teflate compounds are also similar to fluorides. For example,  $\text{As}(\text{OTeF}_5)_3$  resembles  $\text{AsF}_3$  in its ability to form adducts with simple Lewis bases ( $\sigma$ -acidity) and to form complexes with low-valent transition metals ( $\pi$ -acidity) [12]. As in binary fluorides, the teflates can exchange the  $\text{OTeF}_5^-$  anion between donor and acceptor teflates [13].

The versatility of teflates have prompted the development of other highly electronegative ligands such as  $(\text{O})\text{F}_4\text{I}-\text{O}^-$  [14]. The principle of electronegative ligands can be extended to polydentate ligands. Recently, cis- and trans- $(\text{HO})_2\text{TeF}_4$  have been reported and the first derivatives including a xenon compound are available [15]. Sym- $(\text{HO})_3\text{TeF}_3$  [16] and  $\text{H}_2\text{N}-\text{TeF}_5$  [17], open up new directions for research. Following the analogy of organo-fluorocarbons, organo-teflate chemistry is just now being developed [18]. The promising chemistry of teflate is still very much in its early stages.

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## Models for Hemocyanin and Tyrosinase

Richard J. Sullivan

Literature Seminar

May 14, 1986

A problem encountered in the study of biological systems is that detailed investigations are often hampered by the lack of a high resolution crystal structure. Proteins and enzymes are often exceedingly difficult to crystallize due to their large size and complex structure. This situation is certainly the case with the oxygen-carrying protein hemocyanin (Hc) and the mono-oxygenase tyrosinase (Tyr).

Hemocyanin (1) serves as the oxygen carrier in the hemolymph of arthropods (crabs, lobsters, etc.) and molluscs (snails, clams, octopus, etc.). It is well known that the active site of Hc consists of a binuclear copper center that binds oxygen reversibly [1]. The oxygen-coordinated form of the Hc(oxyHc) and its derivatives have been studied extensively [2]. The present active site picture for oxyHc and metHc (figure 1) has arisen from the combination of resonance Raman [3], Extended X-ray Absorption Fine Structure (EXAFS) [4], magnetic susceptibility [5], and electronic absorption [6] studies. The salient features of oxyHc are the 1,2- $\mu$ -peroxo bridge and the endogenous bridge which is believed to mediate the strong antiferromagnetic coupling.

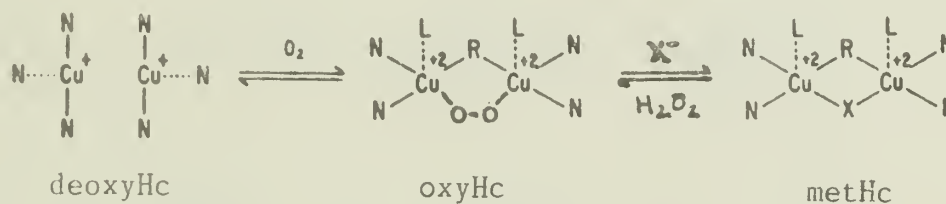


Figure 1. Possible active site picture for hemocyanin.

There is less information available on the active site of deoxyHc because the  $d^{10}$  Cu(I) center is not amenable to many spectroscopic techniques. EXAFS results suggest that each copper center is bound to two [6] or three [4b] imidazole-like ligands. A recent crystal structure of *Panulirus interruptus* deoxyHc shows that each Cu(I) ion is separated by a distance of  $3.8 \pm 0.4 \text{ \AA}$  with three histidine ligands coordinated to each copper [8] (figure 1).

Tyrosinase [9] serves as both a mono-oxygenase and a two electron oxidase in various microorganisms, plants, and animals. It catalyzes the o-hydroxylation of monophenols to catechols (mono-oxygenase activity) and the subsequent oxidation of catechols to o-quinones (oxidase activity). Although Tyr has a different biological function than Hc, comparison of the spectroscopic and chemical properties of these two metalloproteins indicate that the binuclear copper active sites are very similar [10].

Some current model studies have focused on mimicking the magnetic properties of Hc and Tyr. In order to identify the endogenous bridging ligand, Reed and coworkers have utilized an alkoxytetrakis(imidazole) ligand to prepare a diamagnetic 1,3  $\mu$ -azido bridged dicopper(II) complex with a Cu-Cu separation of 3.615 Å. This compound features an "endogenous" alkoxide bridge which is believed to provide the superexchange pathway [11]. Sorrell and coworkers have





synthesized an analogous 1,3  $\mu$ -azido bridged Cu(II) binuclear complex that is diamagnetic and features an "endogenous" phenoxide bridge [12]. The hydroxide ion is also a viable candidate for the "endogenous" bridge [13].

It is known that CO binds to deoxyHc in a terminal fashion with a binding ratio of 1CO/2Cu(I) [14]. Model studies indicate that two coordinate complexes are relatively inert towards CO, whereas related three coordinate complexes readily bind CO [15]. These model studies suggest a possible explanation for the CO binding ratio of deoxyHc [14].

The oxygen binding properties of Tyr and Hc can be modelled by Cu(I) complexes of the binucleating ligand m-XYLpy2 (shown below) [16]. When exposed to oxygen, the aromatic ring of the dicopper(I) complex becomes hydroxylated. A phenoxo and hydroxo Cu(II) binuclear compound forms. Labeling studies show that the phenoxo and hydroxo oxygens are derived from the labeled oxygens [16]. The Cu(II) ions can be leached out of the phenoxo bridged dicopper(II) species to give the free phenol. Reaction of the free phenol with Cu(I) results in the formation of a phenoxo bridged dicopper(I) complex [17]. This complex has been shown to reversibly bind oxygen by visible spectroscopy.

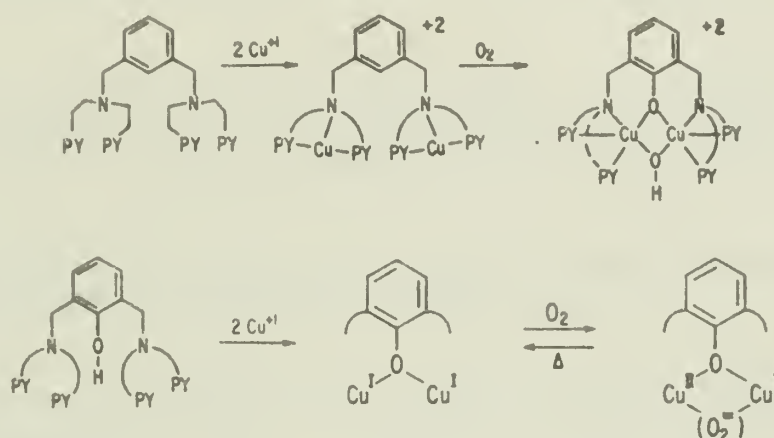


Figure 2. Reaction scheme for m-XYLpy2 as described above.

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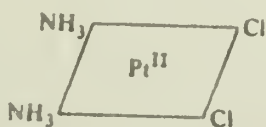
The Chemistry of cis-dichlorodiammineplatinum(II):  
An Anticancer Drug

David W. Conrad

Literature Seminar

May 15, 1986

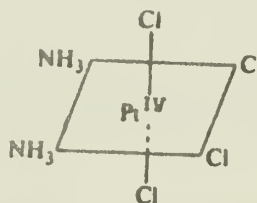
The neutral platinum coordination complex, cis-dichlorodiammineplatinum(II), Peyrone's chloride, was first synthesized in 1845 [1]. It was separated from the corresponding trans isomer by Werner as early as 1898 [1], but it was not until 1969 that its potent anticancer activity was reported. Rosenberg *et al.* [2,3] found that an electric field applied to a suspension of *E. coli* prevented cell division, but induced filamentous growth. This effect was finally traced to the presence of two coordination complexes: cis-dichlorodiammineplatinum(II) and cis-tetrachlorodiammineplatinum(IV) which were produced electrolytically at the platinum electrodes.



cis-dichlorodiammineplatinum(II)

Cisplatin

cis-DDP



cis-tetrachlorodiammineplatinum(IV)

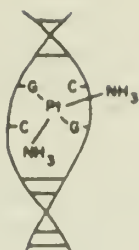
The initial animal studies revealed that both these complexes had antineoplastic activity, while the corresponding trans isomers were inactive [4]. The platinum(II) complex was found to be the more potent and was subjected to clinical trials in 1972. This complex, called cisplatin, is now widely used in the treatment of solid tumors of the head, neck, testes, and ovaries [5].

In order to understand the chemical reactions that occur when cisplatin is injected intravenously, one must consider the aqueous chemistry of the complex. The species formed are highly dependent on the chloride ion concentration in both the plasma and cytoplasm [6]. At sufficiently low chloride ion concentration, cisplatin undergoes a series of stepwise hydrolysis reactions [7]. It is believed that the aquated species are the physiologically active forms. Hydroxo-bridged dimers and trimers can also be formed, but are unlikely to be a major intracellular component due to the low platinum concentration under physiological conditions [8,9,10].

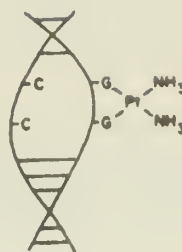
There is currently considerable evidence that DNA is the principal intracellular target for cisplatin [2,3,11]. Inhibition of cell division implies interference with DNA replication, but concomitant cellular growth indicates that RNA and protein synthesis are proceeding normally. Several types of possible DNA-cisplatin adducts have been proposed. These include both DNA interstrand(I) and DNA intrastrand(II) crosslinks. Current evidence from both NMR studies [12] and X-ray crystal structures [13] favors an intrastrand crosslink between N(7) on adjacent guanines as the critical platinum binding lesion. The corresponding trans isomer, due to stereochemical restraints, would be unable to form such a crosslink.







(I)



(II)

Recent kinetics data by Lippard [14] suggest that different Pt-DNA lesions occur for the cis- and trans-isomers. These studies also point to differential repair of these lesions as being responsible for the greatly increased cytotoxicity of the cis- vs. the trans-isomer.

Elucidation of the specific repair mechanisms along with an understanding of the structure activity relationship is leading to the design of more efficient inorganic anticancer drugs.

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Where Are the Protons in  $H_3V_{10}O_{28}^{3-}$ ?

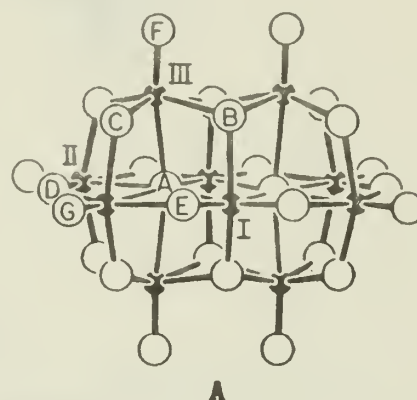
David J. Maltbie

Final Seminar

May 15, 1986

Polyoxoanions form many interesting and unusual complexes which contain covalently bound organometallic species [1]. Unfortunately, it is very difficult to predict or control the binding sites on the polyoxoanions used by the metal centers. In order to take a more rational approach to polyoxoanion reaction chemistry, a better understanding of the charge distribution in polyoxoanions is needed. A good starting point for a study of the reactivity of a polyoxoanion is the identification of its protonation sites.

The  $V_{10}O_{28}^{6-}$  anion (see A) is a good candidate for a protonation study as its solid state structure has been determined x-ray crystallographically [2], and it can be probed in solution using  $^{17}O$  and  $^{51}V$  NMR spectroscopy.  $^{17}O$  NMR is especially useful in the identification of protonation sites as coordination of a cation to an oxygen center results in a large upfield shift of its  $^{17}O$  resonance [3]. Although several spectroscopic studies have been carried out on the  $V_{10}O_{28}^{6-}$  anion [4-8], its behavior in solution and the identity of its protonation sites are not well understood.



In the present investigation, the  $V_{10}O_{28}^{6-}$  anion was characterized in aqueous solution using a series of  $^{17}O[^{51}V]$  NMR experiments. By selectively decoupling the inequivalent vanadium nuclei and observing the effect on the line widths of the oxygen resonances, unique assignments were determined for all the resonances seen in the  $^{51}V$  and  $^{17}O$  NMR spectra of the  $V_{10}O_{28}^{6-}$  anion.

Our approach to the problem of identifying the protonation sites in the  $V_{10}O_{28}^{6-}$  anion was to isolate and characterize its triprotonated analog,  $H_3V_{10}O_{28}^{3-}$  [9]. This anion was isolated as the  $CH_3CN$  soluble salts  $H_3V_{10}O_{28}^{3-}[(n-C_4H_9)_4N]_3$ , 1, and  $H_3V_{10}O_{28}^{3-}[(C_6H_5)_4P]_3$ , 2, by the acidification of an aqueous  $Na_3VO_4$  solution followed by addition of the appropriate counterion. Compound 1 was then characterized in  $CH_3CN$  solution using  $^1H$ ,  $^{51}V$ , and  $^{17}O$  NMR spectroscopy.

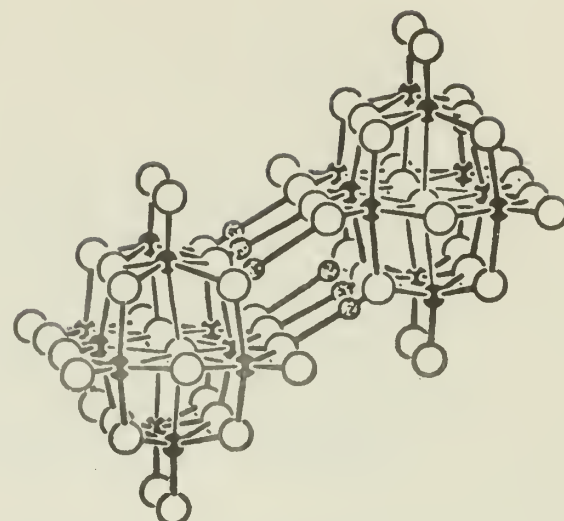
$^1H$  NMR spectroscopy was used to show that the anion in 1 retained its three protons in solution and did not self-condense to form water and an oxo-bridged dimer as seen for other protonated polyoxoanions [10]. The  $^{51}V$  NMR spectrum of 1 demonstrated that the two  $V_I$  centers (see A) are inequivalent in the  $H_3V_{10}O_{28}^{3-}$  anion, and that addition of water to the sample catalyzed proton exchange to give the anion effective  $D_{2h}$  symmetry. Lineshape changes were also seen in the  $^{17}O$  NMR spectrum of 1 upon water addition which were consistent with the occurrence of a water catalyzed proton exchange process. Examination of the lineshape changes showed the only resonances due to the  $O_C$  and  $O_B$  oxygens were significantly affected. These spectra indicated that two protons were associated with the  $O_C$  oxygens and one proton with the  $O_B$  oxygens. To provide additional evidence, selective enrichment experiments were carried out to help in the assignment of the resonances observed in the  $^{17}O$  NMR spectrum of 1.





An x-ray crystallographic study of **2** was performed by Professor Victor W. Day at the University of Nebraska. The protons in the  $\text{H}_3\text{V}_{10}\text{O}_{28}^{3-}$  anion in **2** were crystallographically located, and this anion was found to exist as a hydrogen bonded dimer in the solid state as shown in **B**. Two of the protons in the anion were bound to  $\text{O}_\text{C}$  oxygens and one was bound to an  $\text{O}_\text{B}$  oxygen (see **A**). These results agree with the protonation sites found in solution for the anion in **1**.

As a result of this study we have concluded that the solid state structure of the  $\text{V}_{10}\text{O}_{28}^{6-}$  anion is preserved in solution, and that the triply bridging  $\text{O}_\text{B}$  oxygens and the doubly bridging  $\text{O}_\text{C}$  oxygens are the protonation sites for the  $\text{H}_3\text{V}_{10}\text{O}_{28}^{3-}$  anion in the solid state and in solution.

**B**

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## Fluxional Polyoxoanions

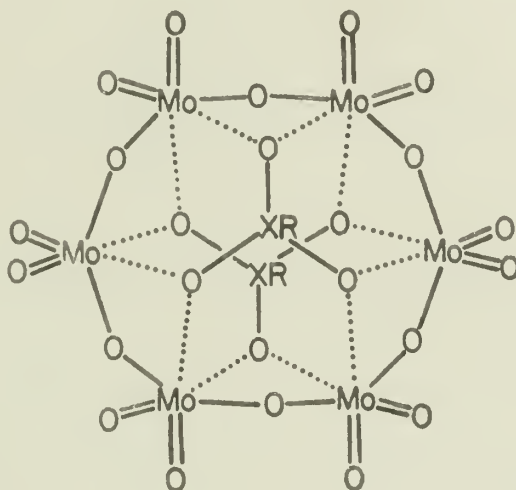
Curtis Schwartz

Final Seminar

May 16, 1986

Although the structural chemistry of the early transition metal polyoxoanions is well established [1], virtually nothing is known about the mechanistic aspects of their chemistry [2]. Despite extensive speculation on the subject, little experimental data is available due largely to the general complexity of polyoxoanion structures as well as the difficulty in synthesizing specific compounds to test mechanistic hypotheses. In order to gain insight into some mechanistic aspects of polyoxoanion transformations,  $^{17}\text{O}$  dynamic NMR line shape analysis,  $^{17}\text{O}$  spin saturation transfer techniques, and  $^{17}\text{O}$  label crossover experiments have been applied to the study of three polyoxoanions:  $\alpha\text{-Mo}_8\text{O}_{26}^{4-}$ ,  $\text{C}_6\text{H}_5\text{AsMo}_7\text{O}_{25}^{4-}$ , and  $(\text{C}_6\text{H}_5\text{As})_2\text{Mo}_6\text{O}_{24}^{4-}$ .

These three anions share the common  $[(\text{RXO}_3^{2-})_2(\text{Mo}_6\text{O}_{18})]$  structure shown in a, in which  $\text{RXO}_3^{2-}$  units are the tetrahedral  $\text{C}_6\text{H}_5\text{AsO}_3^{2-}$  and/or  $\text{OMoO}_3^{2-}$  anions connected by weak molybdenum-oxygen bonds to opposite sides of an  $\text{Mo}_6^{(\text{VI})}\text{O}_{18}$  ring. The  $\text{C}_6\text{H}_5\text{AsMo}_7\text{O}_{25}^{4-}$  anion shows two distinct types of fluxional behavior

a

that can be related to the anions structure, a puckered  $\text{Mo}_6\text{O}_{18}$  ring capped on opposite sides by tridentate tetrahedral  $\text{MoO}_4^{2-}$  and  $\text{C}_6\text{H}_5\text{AsO}_3^{2-}$  units. The low temperature process involves  $\text{Mo}_6\text{O}_{18}$  ring inversion accompanied by twisting of the  $\text{C}_6\text{H}_5\text{AsO}_3^{2-}$  subunit and twisting or flipping of the  $\text{MoO}_4^{2-}$  subunit. Only weak ( $>2.2$  Å) molybdenum oxygen bonds are broken and reformed. The higher temperature process, although mechanistically undefined, involves cleavage of stronger (1.7-2.0 Å) molybdenum-oxygen bonds. Evidence is presented for related processes in the  $\alpha\text{-Mo}_8\text{O}_{26}^{4-}$  and  $(\text{C}_6\text{H}_5\text{As})_2\text{Mo}_6\text{O}_{24}^{4-}$  anions.

Two structural features in a are of central importance since they are features observed in numerous other early transition metal polyoxoanion structures. First, the tetrahedral  $\text{PO}_4^{3-}$  ion is a subunit of the Keggin anion  $\text{PMo}_{12}\text{O}_{40}^{3-}$  [3],



the Dawson anion  $P_2Mo_{18}O_{62}^{6-}$  [4], and numerous related species. Second, neutral  $Mo_nO_{3n}$  rings are found in many structures such as the  $P_2Mo_5O_{23}^{6-}$  [5], and  $(CH_3)_2AsMo_4O_{15}H^{2-}$  anions [6]. Therefore, an understanding of the dynamic behavior in the structure shown in a has direct relevance to numerous other systems, and will be discussed.

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# Model Chemistry on Metal Surfaces: Synthesis, Structure and Reactivity Studies of Tungsten-Osmium Mixed-Metal Clusters

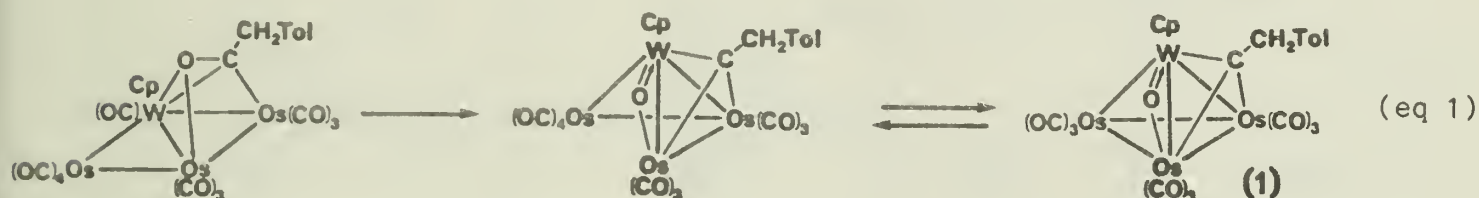
Yun Chi

Final Seminar

June 5, 1986

Recent interest in the chemistry of cluster compounds results from the belief that clusters may serve as models for metal surfaces.<sup>1</sup> Cluster bound alkylidyne, vinylidene, alkylidene, alkyne, alkene and hydride groups are of particular importance due to their implicated role in catalytic processes of metal surfaces.<sup>2</sup> Currently mixed-metal clusters are also under intense scrutiny, because of the advantages of enhanced reactivity and selectivity over their homonuclear counterparts.<sup>3</sup>

$\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$ , **1**, a complex with triply bridging alkylidyne and doubly bridging oxo ligands has been prepared from pyrolysis of  $\text{CpWOs}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol}]^4$  by loss of two equivalents of  $\text{CO}$ .<sup>5</sup> Compound **1** undergoes monocarbonylation to give  $\text{CpWOs}_3(\text{CO})_{10}(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$ , which is an intermediate in the acyl C-O bond scission process (eq 1). Reaction of **1** with phosphorus donors generates both addition and substitution products:

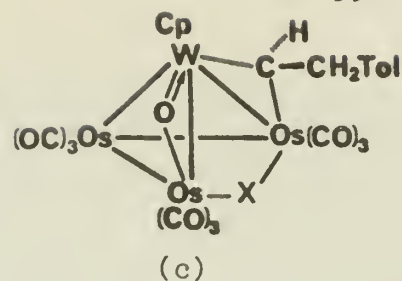
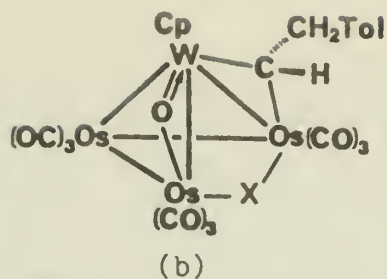
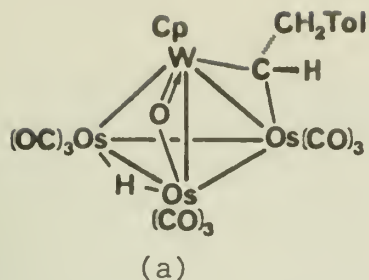


Treatment of **1** with diphenylacetylene provides a butterfly cluster  $\text{CpWOs}_3(\text{CO})_8(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})(\text{C}_2\text{Ph}_2)$  with retention of the alkylidyne functional group and addition of alkyne ligand. This complex undergoes reaction under an  $\text{H}_2$  atmosphere, or decarbonylation to give  $\text{CpWOs}_3(\text{CO})_7(\mu\text{-H})_2(\mu\text{-O})(\mu_4\text{-}\eta^2\text{-CCHTol})\text{-}(\text{CPh=CHPh})$  or  $\text{CpWOs}_3(\text{CO})_7(\mu\text{-O})(\mu\text{-}\eta^2\text{-CHCHTol})(\text{C}_2\text{Ph}_2)$ , respectively. The former represents the only example of alkylidyne to vinylidene transformation under an  $\text{H}_2$  atmosphere; the latter reacts with  $\text{CO}$  inducing coupling between coordinated alkyne, and alkenyl moieties (which arises from alkylidyne by means of a 1,2-hydrogen migration) to form two butadienyl complexes  $\text{CpWOs}_3(\text{CO})_8(\mu\text{-O})[\text{C(Ph)=C(Ph)CH=CHTol}]$  (which exists as isomers).

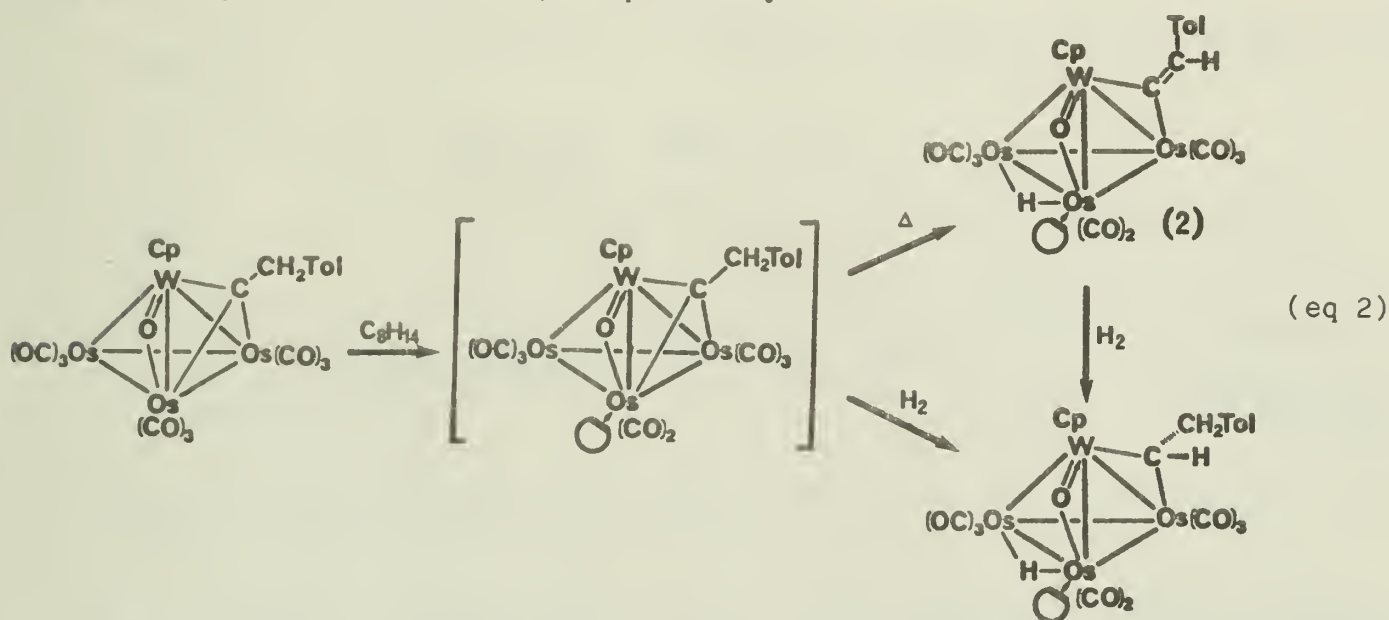
Reaction of **1** with various  $\text{HX}$  reagents,  $\text{X} = \text{H}, \text{Cl}, \text{Br}$  and  $\text{SC}_6\text{H}_5$ , provides three alkylidene complexes with the formulation of  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-X})(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})$  (isomers a, b and c). In the case of the hydrido-alkylidene all three isomers have been observed,<sup>6</sup> the interconversion of isomers a and b and c, involving H-migration and alkylidene isomerization, respectively. For the other alkylidene complexes,  $\text{X} \neq \text{H}$ , only b isomers and c isomers are isolated, of which isomer c is the thermodynamically more stable form. Treatment of  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-Cl})(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})$  (isomers b and c) with gaseous  $\text{BCl}_3$  generates  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-Cl})(\mu\text{-OBCl}_3)(\mu\text{-CHCH}_2\text{Tol})$  in which  $\text{BCl}_3$  has been found to coordinate the bridging oxo-ligand, thereby activating the reverse alkylidene isomerization from isomers-c to b. The structures of a, b and c are confirmed by the structural studies on  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})$ ,<sup>7</sup>  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-Cl})(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})$ , and  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-Cl})(\mu\text{-OBCl}_3)(\mu\text{-CHCH}_2\text{Tol})$ , respectively.







Reaction of 1 with cyclooctene under  $N_2$  or  $H_2$  atmosphere affords  $CpWOs_3(CO)_8(C_8H_{14})(\mu-H)(\mu-O)(\mu-CCH_2Tol)$ , 2, or  $CpWOs_3(CO)_8(C_8H_{14})(\mu-H)(\mu-O)(\mu-CHCH_2Tol)$ , respectively. The reaction presumably proceeds by cyclooctene substitution to give an alkylidyne intermediate  $CpWOs_3(CO)_8(C_8H_{14})(\mu-O)(\mu_3-CCH_2Tol)$ ; the interconversion between the alkylidene, vinylidene and alkylidyne species are discussed (eq 2). Furthermore, each  $C_8H_{14}$  substituted alkylidene and vinylidene complex exists as two isomers in solution resulting from H-migration and vinylidene "rotation", respectively.



Compound 2 undergoes olefin exchange with ethylene to provide  $CpWOs_3(CO)_8-(C_2H_4)(\mu-H)(\mu-O)(\mu-CCH_2Tol)$ , for which an X-ray diffraction study reveals an unusual feature in that the  $C_2H_4$  group is coordinated to an Os atom associated with the bridging hydride. The reversible  $C_2H_4$  insertion into Os-H-Os bond and its reverse,  $\beta$ -hydride elimination,<sup>8</sup> has been established by dynamic NMR techniques. Exchange with either *cis* or *trans*- $C_2H_2(CO_2CH_3)_2$  gives another extreme of such olefin insertion reaction, an alkyl complex  $CpWOs_3(CO)_8(\mu-O)(\mu-CCH_2Tol)[CH-(CO_2CH_3)CH_2(CO_2CH_3)]$  being isolated, as demonstrated by an X-ray diffraction study.

The related insertion of an alkyne into the Os-H-Os bond has also been discovered by exchange of  $C_8H_{14}$  with diphenylacetylene to give  $CpWOs_3(CO)_8(\mu_3-O)-(\mu_3-\eta^2-CCH_2Tol)(\mu-\eta-CPh=CHPh)$ , which has been structurally characterized. Subsequent reaction with  $C_8H_{14}$  regenerates 2, suggesting that the insertion of the alkyne is reversible. Reaction with  $CpW(CO)_2(CTol)$ , equivalent to be an alkyne by the isolobal analogy, provides a TBP pentanuclear cluster  $Cp_2W_2Os_3(CO)_9(\mu_3-O)(\mu_3-\eta^2-CCH_2Tol)$ . Variable temperature NMR studies show that the vinylidene ligand undergoes a one-third cycle of circumambulation, as indicated in the theoretical calculation by Hoffmann on  $M_3(\mu_3-\eta^2-C=CH_2)$  systems.<sup>9</sup>



Finally, an attempt was made to optimize conditions for the synthesis of  $\text{CpWOs}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol}]$  from the reaction of  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  with  $\text{CpW}(\text{CO})_2\text{-(CTol)}$ , in which three mixed-metal compounds are formed, i.e.,  $\text{CpWOs}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol}]$ ,  $\text{CpWOs}_3(\text{CO})_{10}(\mu_3\text{-CTol})_2\text{H}^{10}$  and  $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_7(\mu_3\text{-}\eta^2\text{-C}_2\text{Tol}_2)$ .<sup>11</sup> This effort resulted in the isolation of a fourth  $\text{WOs}_3$  cluster  $[\text{CpW}(\text{CO})_3](\mu\text{-H})_2\text{Os}_3\text{-(CO)}_9(\mu_3\text{-CTol})^{12}$ , which has been identified as an intermediate in the formation of  $\text{CpWOs}_3(\text{CO})_{10}(\mu_3\text{-CTol})_2\text{H}$ . Reaction of  $\text{D}_2\text{Os}_3(\text{CO})_{10}$  with  $\text{CpW}(\text{CO})_2(\text{CTol})$  reveals a remarkable isotope effect which is manifested in the increased yield of deuterated  $\text{CpWOs}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-C(O)CD}_2\text{Tol}]$ , from 26% to 49%. Pyrolysis of  $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_7(\mu_3\text{-}\eta^2\text{-C}_2\text{Tol}_2)$  initiates a reversible alkyne C-C bond scission to give  $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_5(\mu\text{-CTol})(\mu_3\text{-CTol})$ .<sup>13</sup>

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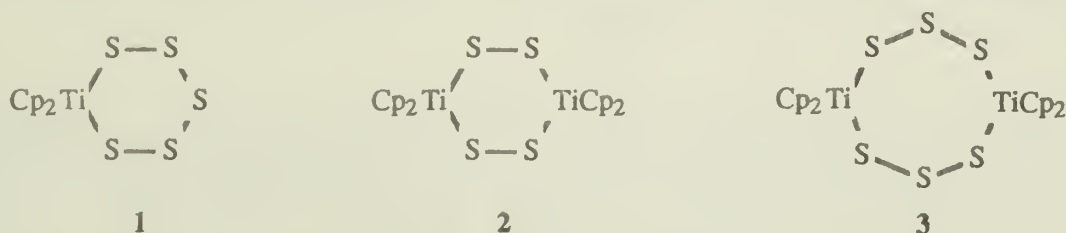
## Synthesis and Reactivity of Some Organometallic Chalcogenide Complexes

Dean M. Giolando

Final Seminar

July 22, 1986

The research reported today has been motivated by a desire to understand the reaction chemistry of polysulfido complexes [1]. The polysulfide ligands contain catenated sulfur atoms, and as such resemble elemental sulfur. The question being addressed is whether these ligands exhibit chemistry similar to that of the element. The reaction of sulfur with nucleophiles (such as phosphines and sulfide anion) is a classic reaction [2]. Under vigorous conditions sulfur and electrophilic acetylenes react in the vapor phase [3]. Our studies into analogous reactivity have centered upon the titanocene pentasulfide (1) complex.



Compound 1 is rapidly desulfurized by tertiary phosphines to give dititanium polysulfides (1,4-[Cp<sub>2</sub>Ti]<sub>2</sub>S<sub>4</sub> (2) [4] and 1,5-[Cp<sub>2</sub>Ti]<sub>2</sub>S<sub>6</sub> (3) [5]). Our results indicate the Ti<sub>2</sub>S<sub>4</sub>/Ti<sub>2</sub>S<sub>6</sub> product distribution arises from the competition between coupling of two (RC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>TiS<sub>3</sub> units and further desulfurization of (RC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>TiS<sub>3</sub> by PR<sub>3</sub>. The synthesis of 1,4-[Cp<sub>2</sub>Ti]<sub>2</sub>S<sub>4</sub> from an intermediate perthiocarbonate compound, Cp<sub>2</sub>TiCS<sub>4</sub>, may occur as well from an unstable Cp<sub>2</sub>TiS<sub>2</sub> species; which is probably also true for the oxidative-coupling of Cp<sub>2</sub>Ti(SH)<sub>2</sub>.

The presence or existence of reactive titanocene sulfides is suggested by the formation of dithiolene complex (Cp<sub>2</sub>TiS<sub>2</sub>C<sub>2</sub>(CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>) by addition of PR<sub>3</sub> to a solution of 1 and CH<sub>3</sub>O<sub>2</sub>CC≡CCO<sub>2</sub>CH<sub>3</sub> (DMAD). In this case, PR<sub>3</sub> probably reacts with 1 to give a polysulfido-phosphonium intermediate which upon reaction with the electrophilic acetylene gives the observed dithiolene product, even at -20°C. The reaction of a tertiary phosphine and 1 is similar to the reaction of sulfide in that both involve an initial ring opening step to afford ionic open chain intermediates.

In the presence of unhindered ketones Cp<sub>2</sub>TiS<sub>5</sub> (1) reacts with sulfide anion, S<sup>2-</sup>, to give 1,4-Cp<sub>2</sub>TiS<sub>4</sub>CR<sub>2</sub> heterocycles. Both the 1,3- and 1,4-Cp<sub>2</sub>TiS<sub>4</sub>CH<sub>2</sub> isomers are produced when CH<sub>2</sub>Br<sub>2</sub> is used. The pathway for the substitution of a sulfur atom for a CR<sub>2</sub> unit into the cyclo-TiS<sub>5</sub> moiety is proposed to proceed via initial cleavage of the TiS<sub>5</sub> ring by an anionic sulfur nucleophile. The intermediate (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiS<sub>x</sub><sup>2-</sup> species would be capable of nucleophilic addition to ketones or substitution on alkyl halides.



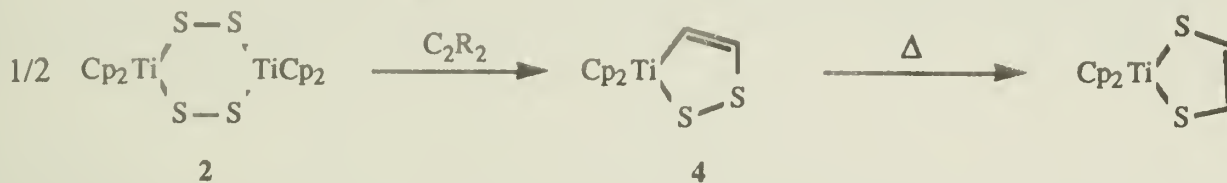






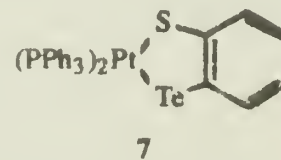
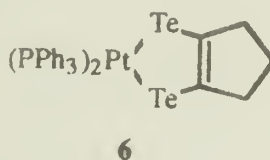
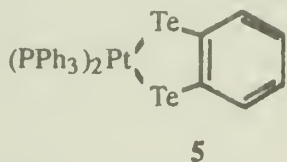
In the reactions of **1** with nucleophiles the titanium center functions as a template. Direct reaction at the titanium atom may not be mechanistically important. Rather, the Ti-S bonds provide stabilization of the reactive polysulfido compounds produced. We also suggest that the reaction is occurring predominantly at the S(2)-S(3) site.

The compounds  $(RC_5H_4)_2TiE_5$  ( $R=H, CH_3$ ;  $E=S, Se$ ) [6] have been reported to react with the activated acetylene DMAD to afford alkenedichalcogenide (dithiolene and diselenene) complexes. Through studies on 1,4- $[(MeCp)_2Ti]_2S_4$  we have found that these reactions occur via the intermediacy of a vinyldisulfide compound,  $Cp_2TiSC_2(CO_2CH_3)_2S$  (**4**). This intermediate undergoes an intramolecular



rearrangement to afford the dithiolene. The reason that the vinyldisulfide had not previously been identified in the pentasulfide chemistry is attributable to the high activation energy associated with the addition of DMAD to the poorly nucleophilic  $(RC_5H_4)_2TiS_5$ . Another example of a migration reaction is found in the rearrangement of  $(C_5H_5)_2TiS_5$  to  $(C_5H_5)TiS_5C_5H_5$ . This reaction also provides a third example of structural isomers in titanium sulfide chemistry.

One goal in this project was the synthesis and characterization of the tellurium (ditellurene) analogs of dithiolenes. Interest in this class of coordination compounds can be traced to the recent synthesis of the tetratellurifulvalenes [8,9]. The compounds  $(RC_5H_4)_2TiE_2C_2R_2$  ( $E = S, Se$ ) have been observed to transfer their chelate to other metal centers [6] and it seems plausible that the tellurium derivatives would behave similarly. However, our attempts to synthesize titanocene telluride complexes failed. We were able to produce the first examples of ditellurene complexes by turning to the robust  $Pt(II)(PPh_3)_2$  system. Using reported procedures the ligands  $\underline{o}\text{-C}_6\text{H}_4(\text{TeLi})_2$  [8] and  $1,2\text{-C}_5\text{H}_6\text{TeLi}_2$  [9] were prepared, and found to react readily with  $Pt(PPh_3)_2Cl_2$  to provide  $Pt(PPh_3)_2(\text{Te}_2\text{C}_6\text{H}_4)$  (**5**) and  $Pt(PPh_3)_2(\text{Te}_2\text{C}_5\text{H}_6)$  (**6**), respectively. We have also found  $\underline{o}\text{-C}_6\text{H}_4(\text{SLi})\text{Li}$  [10] to be a precursor to  $Pt(PPh_3)_2(\text{TeSC}_6\text{H}_4)$  (**7**). Compound **5** was structurally characterized.



Soluble and reactive anionic main group sulfides can be prepared by the reaction of sulfide anion,  $S^{2-}$ , and main group sulfides. In this way numerous examples of group IV ( $M_xS_y^{z-}$  and  $R_2MS_2^{2-}$ ,  $M = Ge$  and  $Sn$ ) [11] and group V ( $ES_3^{3-}$  and  $RES_3^{2-}$ ,  $E = P$  and  $As$ ) [12] sulfide anions can now be found in the literature. We have found sila-1,1-dithiolate ( $Me_2SiS_2^{2-}$ ) complexes can be conveniently prepared by treating a solution of  $(Me_2SiS)_3/Li_2S$  with metal dichlorides. Using this methodology the complexes  $Cp_2MS_2SiMe_2$  ( $M = Ti$  (**8**) and  $V$ ) and  $Pt-(S_2SiMe)_2(PPh_3)_2$  were prepared from their respective chlorides.



The titanium compound,  $\text{Cp}_2\text{TiS}_2\text{SiMe}_2$ , is particularly interesting because it contains two potentially reactive sites: the Ti-S and Si-S bonds. The reaction of **8** with transition metal (or main group) dichlorides affords  $\text{Cp}_2\text{TiCl}_2$  (>90%) without the formation of  $\text{Me}_2\text{SiCl}_2$ , indicating that reaction at titanium is preferred.

There has been recent interest in S-for-O exchange reactions within the coordination sphere of transition metals. The ability of  $(\text{Me}_3\text{Si})_2\text{S}$  to effect such a transfer with oxometallates has been explored by several research groups [13,14,15]. However the synthetic utility of  $(\text{Me}_3\text{Si})_2\text{S}$  is hampered by reduction (and silation) and declusterification. We have examined the reactivity of  $\text{Cp}_2\text{TiS}_2\text{SiMe}_2$  with oxometallates and observed a sulfiding reaction without reduction. Using **8** we were able to convert  $\text{WO}_x\text{S}_{4-x}^{2-}$  ( $x = 4, 3, 2$ ) and  $\text{TaW}_5\text{O}_{19}^{3-}$  to  $\text{WS}_4^{2-}$  and  $\text{TaW}_5\text{O}_{18}\text{S}^{3-}$ , respectively.

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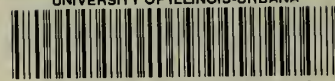








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